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EFFECT OF FUEL ADDITIVES ON THE CHEMICAL AND PHYSICAL CHARACTERISTICS OF PARTICULATE EMISSIONS IN AUTOMOTIVE EXHAUST

John B. Moran, et al

Dow Chemical Company

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Effect of Fuel Additives on the Chemical and Physical Characteristics of Particulate Emissions in Automotive Exhaust

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by

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Midland, Michigan 48640

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FINAL REPORT

June 1972

EFFECT OF FUEL ADDITIVES ON THE CHEMICAL AND PHYSICAL CHARACTERISTICS OF PARTICULATE EMISSIONS IN AUTOMOTIVE EXHAUST

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Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Attention: Dr. Jack Wagman
Project Officer

Contract CPA-22-69-145

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FINAL TECHNICAL REPORT

July 1969 to May 1972

for

Division of Chemistry and Physics
Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Attention: Dr. Jack Wagman, Project Officer

FOREWORD

This report was prepared by the Transportation Research Group, Ag-Organic Chemicals Department, The Dow Chemical Company, Midland, Michigan, as fulfillment of Contract CPA-22-69-145 and extensions thereto. This work was administered under the direction of the Division of Chemistry and Physics, Environmental Protection Agency, with Dr. Jack Wagman as Project Officer.

This report covers work performed from July 30, 1969, to May 1, 1972. This report was submitted by the authors; John B. Moran, Michael J. Baldwin, Otto J. Manary, and Joseph C. Valenta, in July 1972.

ABSTRACT

This report describes work carried out on a research study to develop methods of generating, collecting, and analyzing particle emissions from automotive power plants by means sufficiently accurate and reproducible to allow the determination of the effect of fuel additives, fuel composition, engine and vehicle operating mode, and advanced emissions control hardware (limited in scope) on exhaust particle size, concentration, and composition. An interim report covering the first year's work was submitted on July 30, 1970.

In this study, we have examined particle emissions from several different engines, loaded by an engine dynamometer, and several different vehicles operated under cruise conditions, the FTP (California) cycle, and the LA-4 cycle. Particle mass measurement techniques have included tailpipe measurement methods and air dilution sampling methods using impaction separators, filters, a Beta-gauge technique, and piezoelectric crystal techniques.

Several different fuel compositions and fuel additions have been examined for their effect on particle emissions. Catalytic exhaust gas reactors have also been evaluated for such effects on a limited basis.

The data gathered substantiates the applicability and validity of the techniques ~~developed~~ and, ~~in~~ addition, suggest a very significant effect of fuel additives, primarily TEL, and to a limited extent exhaust catalytic reactors on exhaust particle size, concentration, and composition. The applicability of the techniques to cycled vehicle studies has been shown.

For clarity of presentation, the above studies which represent the first two year effort in this program are detailed in Part 1 of this report. Part 2 of the report covers the work accomplished in the last half year of the effort and includes an investigation of selected dilution tube variables on the physical and chemical characteristics of particulate exhaust emissions, an ~~evaluation of~~ the particulate collection capabilities of a second Beta-gauge instrument, and ~~detailed analyses~~ of some thirty commercial gasoline samples procured from three different geographical regions of the United States. were analyzed.

TABLE OF CONTENTS

Page

FOREWORD i

ABSTRACT ii

I. INTRODUCTION 1

II. CONCLUSIONS 4

PART I

III. EXPERIMENTAL PROCEDURES 11

- A. Particle Generation 11
  - 1. Engine Dynamometer Studies 11
  - 2. Chassis Dynamometer Procedures 13
- B. Particle Collection 16
  - 1. Proportional Sampling Systems 21
  - 2. Andersen Sampler/Filter 22
  - 3. Total Dilute Filter 22
  - 4. Piezoelectric Crystal 23
  - 5. Beta-Gauge 25
- C. Analysis 25
  - 1. Fuels 25
  - 2. Oils 25
  - 3. Diluent Air 27
  - 4. Exhaust Gases 27
  - 5. Combustion Chamber Deposits 31
  - 6. Exhaust Particles 31

D. Analytical Methods 32
  1. Optical Microscopy 32
  2. Transmission Electron Microscopy (TEM) 32
  3. Scanning Electron Microscopy (SEM) and X-ray Fluorescence 33
  4. X-ray Diffraction 35
  5. Mass Spectrometry 35
  6. High Resolution Mass Spectrometric Analysis .. 39
  7. Neutron Activation 40
  8. Atomic Absorption 44
  9. Emission Spectrometry 46
  10. Polarography 52
  11. Organic Separation 60
    a. Determination of Benzene Solubles and Ultraviolet Absorptivity 61
    b. Determination of Phenolic Content 66
    c. Determination of Acidity 71
    d. Ultraviolet Fluorescence 79

IV. EXPERIMENTAL RESULTS 84
  A. Introduction 84
  B. Engines and Vehicles 84
  C. Dilution Tube 87
    1. Dilution Ratios 87
    2. Dilution Tube Profile - Sampling Zone 87
  D. Test Fuels and Oil 105
    1. Physical Properties 105
  E. Combustion Chamber Deposits 108
  F. Exhaust Gases 108

G. Particulate 113
  1. Mass Emission Rates 113
  2. Mass Distribution 113
  3. Major Element Distribution 120
  4. HCl, NH_3, and H_2O 120
  5. Trace Metal Analysis 120
  6. Crystalline Species 129
  7. Particle Morpheus 131
  8. Organics 165
V. DISCUSSION OF RESULTS 182
VI. FUTURE 208
REFERENCES 209

PART II

I. CONCLUSIONS 211
II. EXPERIMENTAL PROCEDURE 213
  A. Fuel Characterization 213
  B. Evaluation of Dilution Tube Variables on the Collection of Exhaust Particulate Matter 213
    1. Variation of Dilution Tube Flow Rate 216
    2. Effect of Dilution Air Cooling 216
  C. Evaluation of Beta-Gauge Particulate Mass Measuring Device 220
III. EXPERIMENT RESULTS 223
  A. Fuel Characterization 223
  B. Evaluation of Dilution Tube Variables on the Collection of Exhaust Particulate Matter 223
  C. Evaluation of Beta-Gauge 234

IV. DISCUSSION OF RESULTS 238

A. Evaluation of Dilution Tube Variables on the Collection of Exhaust Particulate Matter 238

B. Evaluation of Beta-Gauge Particulate Mass Measuring Device 242

APPENDIX A 244

APPENDIX B 278

APPENDIX C 300

APPENDIX D 314

LIST OF TABLES

Page

1. New Engine Break-in Procedure 11
2. Test Engine Conditioning Sequence 13
3. Vehicle Test Procedure - Chassis Dynamometer 14
4. Exhaust Particle Sample Sources 19
5. Proportional Sampling System for Air-Diluted Exhaust 21
6. D_{50} Value - Andersen Model 0203 22
7. Preparation of Standard Solutions 49
8. Analytical Line Pairs 49
9. Representative Precision and Accuracy 53
10. Run Number Designation 85
11. Test Engines and Vehicles 86
12. Dilution Tube Air-Exhaust Ratios and Flow Rates 88
13. Dilution Tube Sampling Zone Temperature 91
14. Dilution Tube Flow Profile - Chassis Dynamometer 95
15. Dilution Tube Flow Profile - Run 44 95
16. Dilution Tube Mass Profile at Sampling Zone 96
17. Particulate Mass Collected by Andersen Samplers 97
18. Particulate Mass Collected by 4 cfm Filters 98
19. Physical Analysis of Test Fuels 106
20. Test Fuel Trace Metals Content 107
21. Engine Oil Physical properties 105
22. Trace Metal Analysis of New Engine Oil 108
23. Used Engine Oil Trace Metal Analysis 109
24. Combustion Chamber Deposits 110
25. Combustion Chamber Deposits Analysis 111
26. Engine Combustion Chamber Deposits - Trace Metals 112
27. Exhaust Gas Condensate Aldehydes 113
28. Engine Stand Runs - Particulate Mass Emissions 117
29. Emissions Grams Per Mile Chassis Dynamometer 118
30. Mass Medium Equivalent Diameter Exhaust Particulate ... 119

31. Elemental Mass Medium Equivalent Diameter - Engine Stand 121

32. Fractions of HCl, NH_3, and H_2O Present in Exhaust Particles 122

33. Exhaust Particulate - Trace Metals 127

34. X-ray Fluorescence Analysis 120

35. X-ray Diffraction Analysis of Exhaust Particles 129

36. Relative Organic Level by Size Fraction 166

37. Hydrocarbon Type Analysis 168

38. Percent of Total Ion Content 169

39. Organic Analysis of Collected Exhaust Particulates 175

40. Relative Amounts of UV Absorbing Materials 176

41. Relative Amounts of Fluorescent Material 178

42. Analysis of Benzene Soluble Fraction 179

43. Benzene Extracts of Exhaust Particulates 180

44. Analysis of Particulate Benzene Solubles 181

45. Comparison of Particulate Collected 184

46. Filter Temperature During Sampling Run 185

47. Mass Emission Rates 185

48. Emitted Particulate Mass on 4 cfm Filter 186

49. Total Mass Emission Rates 188

50. Mass Emission Rates for Selected Vehicles 189

51. Mass Emission Rates for Selected Vehicles - Cyclic Operation 190

52. Particulate Mass Emission Rates - Vehicle Cycle 191

53. Effect of Exhaust Catalytic Reactors on Particulate 193

54. Effect of Engine Make on Particulate Emissions 194

55. Engine Run and Analytical Method Reproducibility 197

56. Analyses of Runs 21 and 22 204

57. Gasoline Sample Identification 214

58. Physical Analyses of Gasoline Samples 224

59. Physical Analyses of Gasoline Samples 225

60. Physical Analyses of Gasoline Samples 226

61. Chemical Analyses of Gasoline Samples 227

62. Effect of Dilution Variable on Particulate Mass Emission Rates - Non-Leaded Fuel 228

63. Effect of Dilution Variable on Particulate Mass Emission Rates - 0.5 Leaded Fuel 229
64. Lead and Benzo-α-Pyrene Analysis - 0.5 Leaded Fuel 230
65. Benzo-α-Pyrene Analysis - Non-Leaded Fuel 231
66. Particulate Trace Metal Analysis - Leaded Fuel 232
67. Particulate Trace Metal Analysis - Non-Leaded Fuel 233
68. Evaluation of Industrial Nucleonics Beta Gauge Using 2.66 cc TEL/Gallon 235
69. Evaluation of Industrial Nucleonics Beta Gauge Using 0.5 cc TEL/Gallon 236
70. Evaluation of Industrial Nucleonics Beta Gauge Using Indolene 0 (No Lead) 237

TABLE OF FIGURES

Page

Figure

1 Particulate Sampling Tube 1

2 Flow Diagram for Engine Exhaust Particulate Collection 20

3 Crystal Monitor 24

4 Beta-gauge and Tape Sampler System 26

5 Computer Print-out 30

6 Polarographic Determination of Aldehydes 54

7 Polarographic Determination of Aldehydes 56

8 Polarographic Determination of Aldehydes 56

9 Absorptivity Curve 57

10 Polarographic Determination 58

11 Polarographic Determination 59

12 Difference Spectra of 4-Nitrophenate Solutions 75

13 Spectra Obtained Using Benzene Solubles 75

14 Difference Absorbance of Sodium 4-Nitrophenate in Presence of Benzoic Acid in Methanol 76

15 Difference Absorbance of Sodium 4-Nitrophenate in Presence of Benzoic Acid in Methanol 78

16 Dilution Tube Temperature Profile - Engine Dynamometer 91

17 Dilution Tube Flow Profile - Engine Dynamometer 92

18 Dilution Tube Flow Profile - Chassis Dynamometer 93

19 Dilution Tube Profile - Engine Stand Steady-State Operation 94

20 Tube Temperature Monitor at Sampling Zone - California 7-Mode Cycle - Cold Start 99

21 Tube Temperature Monitor at Sampling Zone - California 7-Mode Cycle - Hot Start 100

22 Tube Temperature Monitor at Sampling Zone - Federal Cycle - Hot Start 101

23 Dilution Tube Flow Monitor at Sampling Zone - California 7-Mode Cycle - Hot Start 102

24 Dilution Tube Flow Monitor at Sampling Zone - California 7-Mode Cycle - Cold Start 103

25 Dilution Tube Flow Monitor at Sampling Zone - Federal Cycle - Hot Start 104

26 Percent Change in Total and Saturated Hydrocarbon Emissions from 0 to 75 Hours 114

27 Percent Change in Nitric Oxide Emissions from 0 to 75 Hours 115

28 Percent Change in Carbon Monoxide Emissions from 0 to 75 Hours 116

Exhaust Particulate on Andersen Plates by

29 OM From Run #9 135

30 OM From Run #8 136

31 OM From Run #15 137

32 OM From Run # 11 138

33 TEM From Run # 13 139

34 TEM From Run #2, Plate #1 140

35 TEM From Run #2, Plate #6 141

36 TEM From Run #2 142

37 SEM From Run #1 143

38 SEM From Run #2 144

39 SEM From Run #2, Plate #6 145

40 SEM From Run #2, Plate #1 146

41 SEM From Run #1, Plate #1 147

42 SEM From Run #1, Plate #1 148

43 SEM From Run #21, Plate #1 149

44 SEM From Run #21, Plate #1 150

45 SEM From Run #42, Plates 1, 4, and 7 151

46 X-Ray Spectrum, Run 21 152

47 X-Ray Spectrum, Run 21, Plate 1 152

48 X-Ray Spectrum, Run 21, Plate 1 153

49 X-Ray Spectrum, Run 21, Plate 7 153

50 X-Ray Spectrum, Run 21, Final Filter 154

51 X-Ray Spectrum, Filter Blank 154

52 X-Ray Spectrum, Run 24, Plate 1 155

53 X-Ray Spectrum, Run #24, Plate #4 155

54 X-Ray Spectrum, Run #25, Plate #1 156

55 X-Ray Spectrum, Run #25, Plate #4 156

56 X-Ray Spectrum, Run #25, Plate #7 157

57 X-Ray Spectrum, Run #25, Filter 1 157

58 X-Ray Spectrum, Run #25, Filter 2 158

59 X-Ray Spectrum, Run #25, Filter 3 158

60 X-Ray Spectrum, Run #39, Plate #3 159

61 X-Ray Spectrum, Run #39, Plate #6 159

62 X-Ray Spectrum, Run #41, Plate #4 160

63 X-Ray Spectrum, Run #41, Plate #7 160

64 X-Ray Spectrum, Run #42, Plate #1 161

65 X-Ray Spectrum, Run #42, Plate #4 161

66 X-Ray Spectrum, Run #42, Plate #7 162

67 X-Ray Spectrum, Run #42, Individual Particle of Figure 49A 162

68 X-Ray Spectrum, Run #42, Individual Particle of Figure 49B 163

69 X-Ray Spectrum, Run #42, Individual Particle of Figure 49C 163

70 X-Ray Spectrum, Run #42, Individual Particle of Figure 49D 164

71 Mass Spectral Profile - Cycle 3 Manifold 171

72 Mass Spectral Profile - Cycle 3 Manifold Repeat 171

73 Mass Spectral Profile - Pipe, in Cycle 3 172

74 Mass Spectral Profile - Pipe, in Cycle 3 Repeat 172

75 Mass Spectral Profile - Pipe, in Cycle 4 173

76 Mass Spectral Profile - Pipe, in Cycle 4 Repeat 173

77 Mass Spectral Profile - Pipe, in Cycle 5 174

78 Mass Spectral Profile - Pipe, in Cycle 5 Repeat 174

79 Ratio RU/RF As Function of A255, Run #20, Extracts of Andersen Plate Filters 200

80 Ratio RU/RF as Function of A255, Run #19, Extracts of Andersen Plate Filters 201

81 Ratio RU/RF as Function of A255, Run #21, Extracts of Andersen Plate Filters 203

82 Ratio RU/RF as Function of A255, Run #22, Extracts of Andersen Plate Filters 203

83 Dilution Tube Cooling Baffle 218

84 Cut-Away View of Cooling Baffle Sleeve 219

85 Test Matrix for the Study of Diluent Air Temperatures on Particulate Matter 221

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I. INTRODUCTION

This is a final report detailing two and one-half years of effort to develop a fundamental understanding of the nature of particle emissions from automotive power plants. In general terms, we have developed reproducible and repeatable generation, collection, and analysis techniques which allow detailed characterization of particle emissions. The effect of fuel composition, fuel additives, cyclic operation, and exhaust catalytic reactors thereon have been determined.

This report covers work performed from July 1969 to May 1972. An interim report covering the period July 1969 to July 1970 has been published.

In Part 1 of this report, the scope of the study has involved several related steps which provide the basis for the evolution of the program employed. Specific steps, in order of their occurrence, are as follows:

1. Engine dynamometer study.
    a. Develop methods to generate representative, repeatable, and reproducible exhaust particles.
    b. Develop methods to collect and classify emitted particles.
    c. Develop methods to analyze emitted particles.
    d. Ascertain effect of fuel additives and fuel composition on emitted particles.

2. Chassis dynamometer study (vehicles).
    a. Same as 1.(a.b.c.d.) above.
    b. Relate vehicle exhaust particles to engine study (1.).
    c. Determine effect of hot cyclic operation on exhaust particles.
    d. Determine effect of cold start cyclic operation on exhaust particles.

- e. Determine effect of exhaust catalytic reactor on exhaust particles.
- f. Determine particle emission rates from several uncontrolled typical vehicles.

3. Exhaust particle mass measurement sampling system development.
    - a. Evaluate several mass measurement methods.
        - 1) Tailpipe
        - 2) Air-diluted
            - a) Beta-gauge
            - b) Piezoelectric crystal
            - c) Proportional filter
    - b. Determine critical sampling factors for exhaust particles.

In order to accomplish the objectives of the program, it was found necessary to begin each specific test run with an essentially new, clean engine and exhaust system; and, that the engine be conditioned with the specific test fuel using mild cyclic conditions for the equivalent of 3000 miles before the particle sampling procedures began. Direct tailpipe sampling of particles was found to be unsatisfactory. As a result, an air dilution system, similar to that employed by Habibi(1), was designed. When a 350 CID engine is operating under 60 mph road load conditions, the dilution tube assembly provides a 12:1 dilution ratio (air:exhaust using one-half the engine exhaust). The dilution tube was designed so that all emitted particles can be collected and classified.

Part 1 of this report, then, covers the procedures employed in the generation, collection, and analysis of exhaust particles from automotive power plants under cruise and cyclic conditions from engines and vehicles. It details the effects of engine make, fuel composition, fuel additives, and catalytic reactors on emitted particles. The results of several particle mass measurement techniques are presented and the reasons for the large differences in apparent particle mass determined are discussed.

Part 2 of the report presents the results obtained when a further particle mass measurement technique (Beta-gauge) was evaluated. It further covers the evaluation of selected dilution tube variables on the physical and chemical character of collected exhaust particulate matter. These variables included temperature of diluent air with cooling ahead of and within the dilution tube after mixing with the exhaust, and diluent air flow rate. A detailed chemical and physical characterization of thirty commercially available gasolines is also presented.

II. CONCLUSIONS

The report covers the results of a diverse program spanning two and one-half years directed toward the objective of developing methods of generating, collecting, and analyzing exhaust particulate from automotive engines. Further, the project has examined the effect of fuel composition, fuel additives, generation factors, and collection systems on particulate emissions. The first year's program was directed toward development of repeatable and reproducible methods of generation, collection, and analysis utilizing dynamometer controlled engines. The remaining time was directed toward expansion of the research effort toward investigation of vehicle variables, cycle effects, collection parameters, particulate mass measurement systems, and to a limited degree, an examination of exhaust catalyst effects.

Many of the conclusions are based upon actual comparisons of data generated in this program. However, these data comparisons are interpreted as trends only and not as quantitative changes. A precise quantitative comparison of the effect of the many variables studied is impractical since:

a) Only limited data points could be generated within the time available consistent with the scope of the contract.

b) Subsequent work has revealed other sampling parameters, consideration of which is necessary in the generation of more exact values. These parameters, discussed in Part II of this report, are of particular significance in the collection of exhaust particulate generated by power sources running on lead-free or low-lead fuels.

The conclusions based on this study follow. The page numbers shown after many of the conclusions refer to the location of data tables upon which they were based.

Particle Generation and Collection

1. A generation, collection, and analysis system has been developed which allowed the assessment of the effect of several fuel factors, fuel additives, driving cycles and exhaust catalysts on emitted exhaust particulated mass and composition. (Page 182)

2. From the standpoint of reproducibility the various approaches for the collection and measurement of exhaust particulate matter can be rated in the following decreasing order of confidence:

    a) Andersen sampler/filter. (Pages 22, 97, 194)

    b) 4 cfm fiber glass-fiber filter. (Pages 98, 195)

    c) Millipore membrane filters - sensitive to atmospheric changes in humidity. (Page 198)

    d) Beta-gauge - good for leaded fuel studies; however, its sensitivity was too low for particulate emissions from non-leaded fuels. (Pages 25, 194, 195)

    e) The piezoelectric crystal monitor gave consistently lower mass emission rates when compared to the Andersen-filter collection technique during cruise mode sampling, and was unreliable during cycling mode operation. (Pages 23, 194, 195)

3. Comparison of the particulate matter collected after air dilution to that collected on a total hot filter at the exhaust pipe shows that the latter technique afforded lower particulate mass emission rates than did the collection of air-diluted particulate matter. Analysis of this collected particulate matter showed that air-diluted exhaust contained significantly higher percentages of organic matter for both non-leaded and leaded gasoline. (Pages 117, 118, 184, 194, 195)

Effects of Test Mode and Engine vs. Vehicle Testing

1. A comparison, across similar engine and fuel types, of engine (on dynamometer stand) and vehicle testing shows:

   a) Engine and vehicle data are similar for particulate mass emission rates using low lead and non-leaded fuel. Vehicle particulate mass emission rates are higher for 3 cc/gal leaded gasoline. (Pages 117, 118, 118a)

   b) Vehicle testing afforded higher particulate organics using leaded fuels but lower levels with non-leaded fuels. (Page 121)

   c) Particulate mass-size distributions were similar for engine and vehicle tests using leaded or non-leaded fuels. (Page 119)

2. The California 7-mode cycle and Federal LA-4 23 minute cycle (FTP) gave higher particulate mass emission rates than did 60 mph steady state (SS) operation, particularly for non-leaded and low lead fuels. A comparison of cold to hot start operation in the California cycle shows that the former resulted in higher particulate mass emission rate than did the latter. (Pages 118, 118a, 191)

Effect of Mileage Accumulation

1. Successive vehicle testing under steady state operating conditions using low lead and non-leaded fuels showed a decrease in the mass of emitted particulate matter as mileage was accumulated over the range of 2,500 miles to 10,000 miles. The vehicle using fully leaded fuel showed an increase in particulate emissions as mileage increased. (Pages 188, 189, 190)

2. Successive testing of the same vehicles using the FTP and California 7-mode testing sequences resulted in a decrease in particulate emissions with increased mileage accumulation (700 to 10,000 miles) for both the cold and hot start test modes except for the vehicle running on fully leaded fuel. The vehicle using the fully leaded fuel under the same testing sequence showed a small decrease in emitted particulate matter with mileage accumulation under the cold start FTP mode. However, a small increase was observed under the hot start FTP conditions as the vehicle mileage increased. (Pages 190, 191)

Particle Analysis

1. In general, as evidenced by transmission scanning electron microscopic examination, the percentage of organics associated with exhaust particulates increased with decreasing particle size. (Page 166)

2. In general, 50 percent of the mass of exhaust particles were smaller than 0.1 micron (MMED). (Page 119)

3. There is no apparent correlation between the aromaticity or saturated hydrocarbon content of the various test fuels studied with the concentration of benzene soluble material in the exhaust particulate matter collected. However, in general the use of non-leaded fuels afforded exhaust particulate containing the highest percentages of benzene solubles. (Pages 175, 179, 180, 181)

Effect of Tetraethyl Lead

1. Increased concentrations of tetraethyl lead (TEL) from trace levels to 3.0 ml/gal resulted in increased particle emissions, increased combustion chamber deposits, and increased hydrocarbon emissions. (Pages 108, 110, 113, 114, 117, 118, 118a)

2. Increased concentrations of TEL from trace levels to 1.5 ml/gal resulted in disproportionate increase in combustion chamber deposits, but an increase in particulate emissions. (Pages 108, 110, 113, 117)

3. A comparison of 91 RON non-leaded and low (0.5 cc/gal) lead fuel indicated that the leaded gasoline afforded higher particulate mass emission rates and combustion chamber deposits. The particulate matter in the case of the low lead fuel contained higher concentrations of trace metals and had a lower MMED than the non-leaded fuel. (Pages 108, 110, 113, 120)

   A similar comparison of 100 RON non-leaded to 100 RON 1.5 cc/gal leaded gasoline showed that the latter fuel afforded higher engine combustion chamber deposits, particulate mass emission rates, and particle MMED. Of the variables studied, TEL had the most pronounced effect on particle size. (Pages 108, 113, 119)

4. Microscopic particle examination indicated that the percentage of organic material associated with exhaust particles increased with decreasing TEL concentration. (Page 166)

Effect of Other Fuel Additives and Engine Oil

1. Lead scavengers had a pronounced effect on exhaust particulate and gaseous emissions, and on combustion chamber deposits. The more effective the scavenger, the lower were the hydrocarbon emission levels and the greater the particulate emission levels (motor mix, EDB, and EDC had been evaluated). EDB appeared the most efficient scavenger. (Pages 108, 113, 117)

2. The use of the amine salt of mixed alkyl phosphates as a detergent additive in 3.0 ml/gal TEL motor mix base fuel, decreased hydrocarbon emission levels, but increased particulate emissions when compared to the base fuel. (Pages 108, 113, 117)

3. The use of N-*n*-butyl-*p*-aminophenol (antifouling agent) as a fuel additive increased both combustion chamber deposits and particulate emissions. This additive resulted in a reduced level of particulate organics. (Pages 108, 113, 117, 165)

4. The use of 2,6-di-*t*-butyl-*p*-cresol (oxidation inhibitor) as a fuel additive afforded a reduced level of combustion chamber deposits and little change in particulate mass emission levels. Particulate organic content was significantly reduced. (Pages 108, 113, 117, 165)

5. The use of Amoco 200 heavy duty motor oil afforded little change in either combustion chamber deposits or particulate emissions. (Pages 110, 113, 117, 118)

6. The use of non-leaded fuels containing no additives afforded particulate matter containing the highest percent concentrations of trace elements. However, on an absolute weight basis, the levels of trace metals associated with exhaust particulate showed an increase with the presence of the various fuel additives studied. Analysis of combustion chamber deposits indicated that their trace metal concentration or mass was affected to only a minor extent by variations in the types of fuel additive studied. (Pages 127, 128)

Effect of a Catalytic Converter

1. The use of a single catalytic exhaust converter resulted in a reduction in the mass of emitted particulate matter during the FTP cold start test sequence. However, an increase in the particuate mass generally resulted during the hot start testing sequences. (Pages 192, 193)

   The use of this control device showed an insignificant effect on particle size. (Page 194)

2. Trace metal levels were found to be higher than in similar runs made without the catalytic exhaust converter. (Pages 127, 128)

3. Total unburned hydrocarbons were significantly reduced in the presence of this oxidation catalyst. No differences in NO_x emissions were observed. (Page 114)

Effect of Fuel Octane Rating

No significant trend in either particulate mass emission rate or combustion chamber deposits was evident from a comparison of 91 RON to 100 RON non-leaded fuel. (Pages 113, 117, 118)

PART 1

10-a

III. EXPERIMENTAL PROCEDURES

A. PARTICLE GENERATION

1. Engine Dynamometer Studies

The test engine was completely disassembled, cleaned, and reassembled according to manufacturer's specifications. It was then mounted on the dynamometer bed plate and attached to a fully instrumented Eaton Dynamatic dynamometer. Appropriate control and sensing devices were attached to the engine. The following procedure (Table 1) was then employed to run-in the new engine, using Indolene HO 30 fuel.

TABLE I

NEW ENGINE BREAK-IN PROCEDURE
(28 hours)

1) Warm up engine to 180°F coolant outlet temperature at 1000 rpm, no load. Set spark advance, timing, and idle according to manufacturer's specifications.
2) Run one hour at 1500 rpm, no load, automatic spark advance and fuel flow. Shut down, retorque cylinder heads, drain and change lubricating oil.
3) Run Cycle 1

RPM	Man. Vac. (In. Hg)	Time (Hr)
1500	15.0	1.0
2000	14.0	1.0
2400	14.0	1.0
2600	14.0	1.0
2000	11.0	1.0
		5.0

4) Run Cycle 2

RPM	Man. Vac. (In. Hg)	Time (Hr)
1500	7.0	0.2
2000	7.0	0.6
2500	7.0	1.0
3000	7.0	1.0
2000	7.0	0.2
		3.0

5) Repeat Cycle 2.

6) Run Cycle 3

RPM	Man. Vac. (In. Hg)	Time (Hr)
2000	WOT*	1.0
2500	WOT	1.0
3000	WOT	1.0
3500	WOT	0.5
2800	WOT	0.5
		4.0 x 4 cycles = 16 hours

*WOT - wide open throttle

7) While engine is hot, run motoring compression and conduct leak-down check.

The engine was removed from the dynamometer, drained, partially dismantled, cleaned, reassembled, and placed back on the dynamometer stand. A typical vehicle exhaust system for the specific test engine was attached to one bank of cylinders. The other bank of cylinders was attached to the dynamometer cell exhaust system. Suitable engine monitors were attached to the engine in order to provide continuous monitoring of oil pressure and temperature, coolant temperature, carburetor air flow rate (using a Meriam Laminar Flow Element 50MC-2-45F) and temperature, etc.

The engine was then run for 75 hours continuously using the following "conditioning" sequence (Table 2) employing the specific test fuel designated for that run. During the conditioning sequence, total unburned hydrocarbons, oxygen, nitrogen, carbon monoxide, carbon dioxide, and oxides of nitrogen were measured at frequent intervals by FID, gas chromatography, chemical absorption, and a Scott NO/NO_2 analyzer, respectively. Air/fuel ratios were also calculated based upon exhaust gas composition.

TABLE 2
TEST ENGINE CONDITIONING SEQUENCE

Cycle	RPM	Time (Min.)	Vac. (In. Hg)	Decay
1	800	2	18.8	--
2	1070	13	16.4	1/2 min.
3	1615	20	17.2	1/2 min.
4	2125	13	14.3	1/2 min.
5	1070	12	16.4	1/2 min.

Sequence repeats after each five cycles.

Following the conditioning sequence, the engine exhaust system was attached to the dilution tube inlet pipe and a 48-hour continuous particle sampling run was begun with the engine operating at 2250 rpm and 17" Hg manifold vacuum (equivalent to 60 mph road-load).

At the termination of the test run, the engine was removed from the dynamometer stand, dismantled, and samples for analysis were removed. The samples included engine oil, and combustion chamber and piston head deposits which were carefully removed, weighed, and stored in glass vials. The engine was completely cleaned, reassembled, and reinstalled on the dynamometer stand.

Subsequent tests did not require the break-in procedure noted in Table 1 unless a new engine was used. If the same engine was used again, the next test series began with the conditioning sequence noted in Table 2 after attachment of a new exhaust system.

2. Chassis Dynamometer Procedures

A Clayton CT-200-0 chassis dynamometer with a variable inertia flywheel assembly was used in all tests conducted under this program. A Chelsa direct-drive Model PLDUP-300A fan was located in front of the test vehicle, and operated at 1750 rpm providing 18,750 scfm air flow. In these tests, the vehicle was operated under approximately 60 mph road-load cruise conditions (2250 rpm - 17" Hg manifold vacuum) and under cyclic conditions of the Federal Test Procedure (old California cycle) and LA-4 procedure driven by a vehicle operator following the cycle on a strip-chart recorder driver aid.

Table 3 indicates specific procedures employed to prepare each vehicle for test run.

TABLE 3
VEHICLE TEST PROCEDURE - CHASSIS DYNAMOMETER

1) General Vehicle Inspection

Exhaust System:

a) Inspect for holes or cracks, dents, and collapse
b) Inspect for leaking joints

Engine, check

a) All fluid levels
b) All coolant hoses
c) Air pump fan, power steering, and belts
d) Check heat riser (if applicable) for fullness of operation
e) Check automatic choke operation and adjustment

2) Engine Analysis and Tune-up

Leak Down Test

a) Remove all spark plugs
b) Determine percent leak down of each cylinder
c) Install recommended, new, and gapped spark plugs, points, and condensor

Scope Check

a) Start engine and allow to warm up for at least 15 minutes

TABLE 3 (contd.)

b) With engine running at fast idle, check
  - Spark plugs
  - Spark plug wires
  - Distributor cap and rotor
  - Coil output
  - Points

c) With engine running at idle, check
  - Dwell
  - Timing

d) With engine running at 1500 and 2400 rpm, check timing advance

e) Carburetor Adjustment
  - Tighten intake manifold and carburetor
  - Install new air cleaner element
  - With engine running at specified idle speed, adjust air to fuel ratio to specifications
  - Make final adjustment on idle speed

f) Recheck all scope patterns for normal appearance

3) Instrumentation and Equipment Installation

Thermocouples - install thermocouples in
a) engine oil - dipstick
b) coolant - upper radiator hose - engine out
c) carb air - air filter element

Vacuum and RPM monitors
a) attach tachometer to ignition coil
b) connect "U" tube monometer to intake manifold
c) install throttle cable (if running under cruise mode)

Wheels
a) remove rear wheels
b) Install test tires and wheel assemblies to insure safe operation

4) Procedure for Cold, Hot Starts, and Engine Temperature Stabilization

Cold Start

a) Place vehicle on the dynamometer rolls, set inertia weights for specific vehicle, and go through the preparation for test as well as the tune-up procedure.

b) Allow at least a 12-hour soak period

c) Connect vehicle tailpipe to dilution tube.

d) Start the vehicle and proceed with the individual test.

Hot Start

Continuation of the cold start only after the engine temperature has stabilized.

Engine Temperature Stabilization

Upon completion of the tune-up procedure the vehicle is started cold and driven a total of 32 highway miles at 60 mph to allow the engine temperature to stabilize. The vehicle is then driven on to the dynamometer rolls and prepared for the test during which time the engine idles for approximately five minutes. When preparation has been completed, the vehicle is placed in gear and the speed is increased to 2250 rpm and the intake manifold vacuum is set at 17.0" Hg by controlling the amount of load imposed on the drive wheels. At the time, when the load and the speed become stabilized, the tailpipe is connected to the dilution tube inlet pipe and sampling is started.

B. PARTICLE COLLECTION

Exhaust particles were collected by two basic techniques, one from each of the two exhaust systems attached to the engine. One exhaust system was sampled with a total exhaust hot filter attached to the tailpipe during two test runs. Normally, the exhaust from this side of the engine was exhausted through the dynamometer cell exhaust system. The other exhaust system particulates were collected after air dilution in a large dilution tube described below.

The total exhaust hot filter consisted of a stainless steel filter holder, capable of holding four 8" x 10" filter papers fitted with nine strip heaters totalling 8720 watts to preheat the holder to 150°F to avoid condensate on the filter media during engine start-up. The filter assembly was attached directly to the exhaust tailpipe by a short connector. The exhaust was pulled through the filtering area of 1.75 sq ft by a Sutorbuilt positive displacement pump capable of 800 cfm at 8" Hg, which was exhausted to the test cell exhaust system.

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Continuation of the cold start only after the engine temperature has stabilized.

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Air dilution and cooling of the exhaust from the other side of the engine was accomplished by a dilution tube 16 inches in diameter and 27 feet in length, with a 90 degree bend section, constructed of extruded polyvinyl chloride (PVC) pipe in several sections with butt joints which were taped during assembly prior to each run (Figure 1). The dilution tube was in a temperature and humidity controlled instrument room with the engine test cell on one side and the chassis test cell on the other so that a simple 180 degree rotation of the inlet section allowed operation of the same tube from either exhaust source.

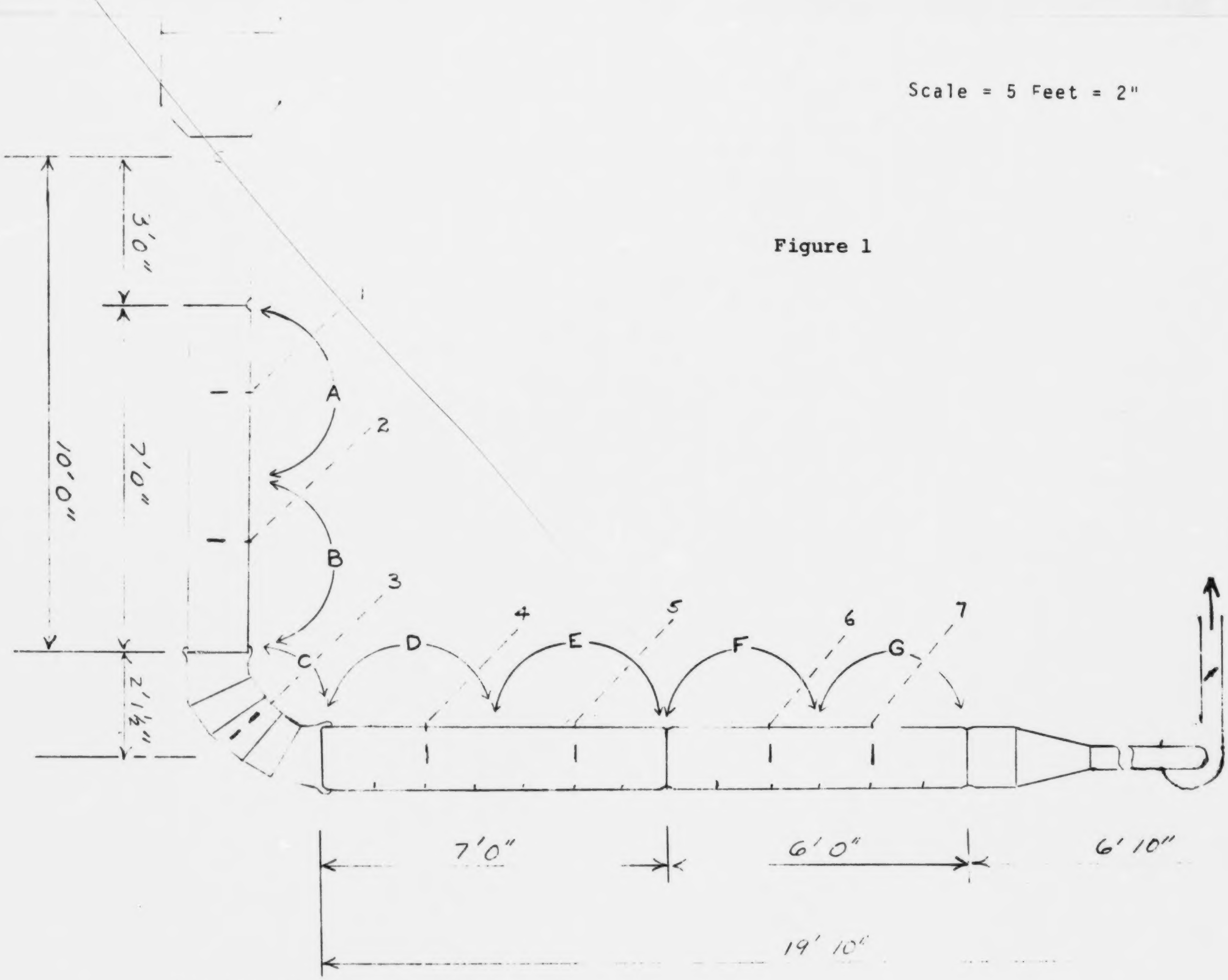
Air was pulled from the dynamometer cell or chassis dynamometer room through a Dri-Pak Series 1100 Class II PIN 114-110-020 untreated cotton filter by a pump at the exit end of the tube at a rate of about 500 cfm. Exhaust was delivered to the tube via a tailpipe extension which was brought into the bottom of the tube downstream of the filter assembly. The extension was bent 90 degrees inside the tube, thus allowing the introduction of the exhaust stream parallel to the tube axis. Within the dilution tube, along the perpendicular plane of the end of the exhaust extension was a mixing baffle which has an 8-inch center hole and was attached to the inside diameter of the tube. The baffle presented a restriction to the incoming dilution air in the same plane as the end of the exhaust extension and performed three essential functions.

a) Provided a turbulent mixing zone of exhaust gas and dilution air.
b) Eliminated engine exhaust pulsations in the tube.
c) Caused the tube to perform as a constant volume device over a wide range of engine exhaust output volumes.

Particle sampling with the dilution tube system was accomplished by two basic methods.

Scale = 5 Feet = 2"

Figure 1


3'0"
7'0"
10'0"
2'1½"
1
2
3
4
5
6
7
A
B
C
D
E
F
G
7'0"
6'0"
6'10"
19' 10"

PARTICULATE SAMPLING TUBE

a) Gravitational fall-out in the tube.
b) Proportional sampling at the extreme end (exit) of the tube.

A schematic of the collection system using the dilution tube is shown in Figure 2.

The gravitational fall-out in the tube provided several discrete samples. First, seven small slits 3/8" x 3" were cut in the bottom of the tube. Special cover glasses were attached to the outside of the tube to collect the material that fell through the slit. The tube was constructed of several sections taped together. Thus, removal of particle samples from each section provided additional discrete samples as a function of distance from the exhaust inlet.

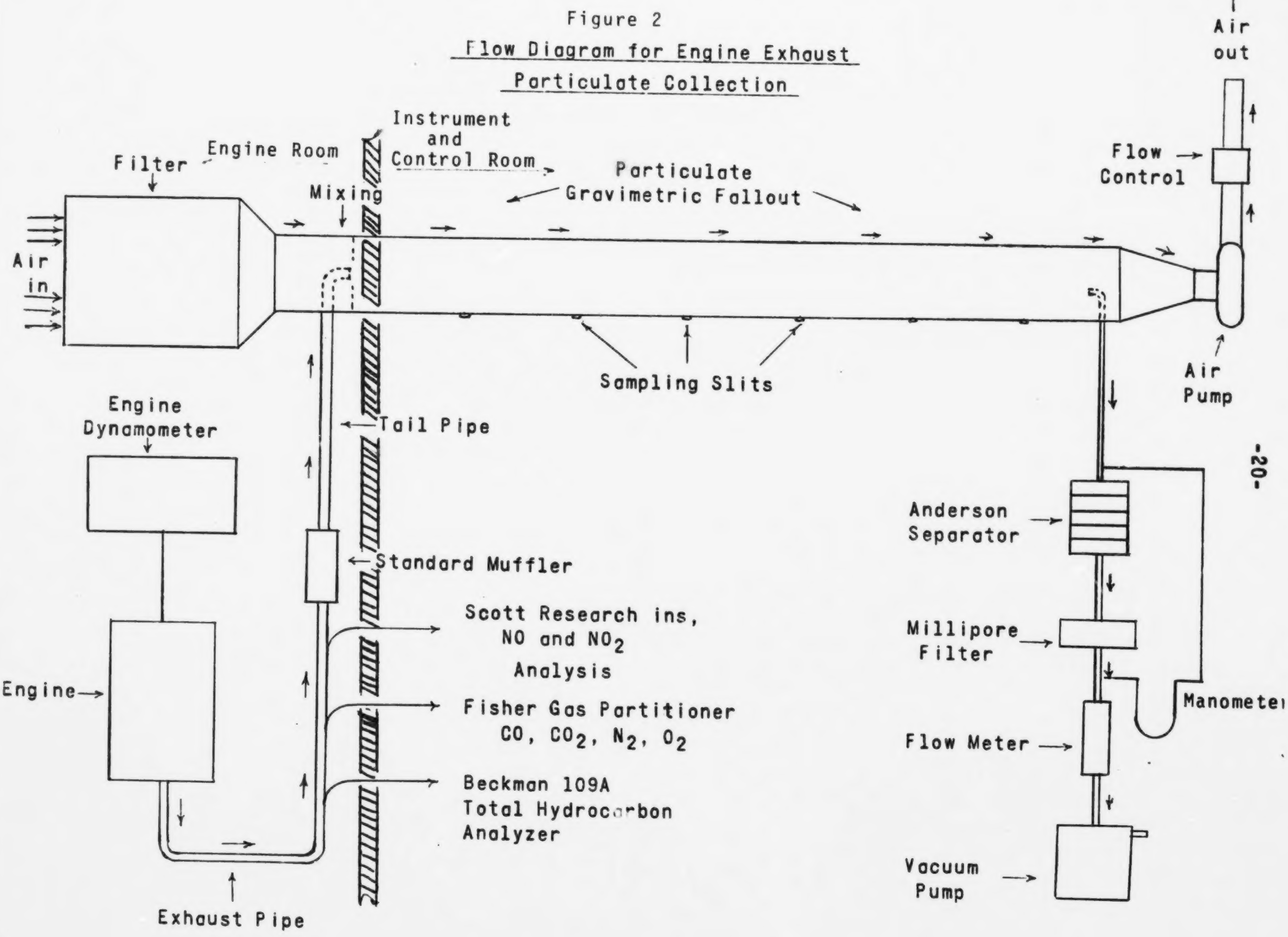
At the extreme end of the tube, a proportional sampling zone was employed to collect particle samples which were still in the air-exhaust stream. Several proportional techniques were employed. These are discussed below. Figure 2 shows the Andersen Impact Sampler (Model 0203) with back-up 142 mm filters. Table 4 summarizes the sample sources.

TABLE 4
EXHAUST PARTICLE SAMPLE SOURCES

Tailpipe:	Total hot exhaust filter
Air Diluted:	Dilution tube
	-slit samples
	-tube sections
	Sampling zone
	-proportional samples

Figure 2

Flow Diagram for Engine Exhaust Particulate Collection


Air out
Air in
Filter
Engine Room
Mixing
Instrument and Control Room
Particulate Gravimetric Fallout
Flow Control
Air Pump
Sampling Slits
Engine Dynamometer
Tail Pipe
Standard Muffler
Engine
Exhaust Pipe
Scott Research ins, NO and NO_2 Analysis
Fisher Gas Partitioner CO, CO_2, N_2, O_2
Beckman 109A Total Hydrocarbon Analyzer
Anderson Separator
Millipore Filter
Flow Meter
Manomete
Vacuum Pump

1. Proportional Sampling Systems

Several proportional sampling systems have been used to determine particle mass and mass-size distribution in the sampling zone of the dilution tube. Each system employed sample pick-up probes of appropriate diameter to provide isokinetic samples from the air-exhaust stream. Pick-up probes entered the tube at right angles, bend inside the tube 90 degrees so that the opening was perpendicular to the tube axis and pointing directly upstream toward the exhaust inlet section. The specific systems used are summarized in Table 5.

TABLE 5
PROPORTIONAL SAMPLING SYSTEMS FOR AIR-DILUTED EXHAUST

System	Sample Flow Rate	Remarks
1) Andersen Model 0203 with 142 mm back-up filter	1 cfm	Provides mass-size distribution. Glass collection plates used. (Used for full run.)
2) Total diluted filter	4 cfm	Total mass only. (Used for full run.) Higher operating temperature than 1.
3) Piezoelectric crystal	1 l/min	Thermo-Systems, Inc. Prototype instrument. (Real time measurements.)
4) Beta-gauge	1 cfm	Tape sampler operated to get total sample. Mass read with Beta-gauge. 20-minute sample.

2. Andersen Sampler/Filter

Andersen Samplers Model 0203 with back-up 142 mm filters were used as the basic particle collection device in these studies. Sample probes sized to deliver an isokinetic sample from the dilution tube were connected to the Andersen Sampler through which a proportional sample was drawn at 1 cfm. The D_{50} cut-off values for the Andersen stages are listed in Table 6.

TABLE 6

D_{50}(2) VALUE - ANDERSEN MODEL 0203

Stage 1	D_{50}	9μ
Stage 2	D_{50}	5.45μ
Stage 3	D_{50}	2.95μ
Stage 4	D_{50}	1.55μ
Stage 5	D_{50}	0.95μ
Stage 6	D_{50}	0.54μ

Preweighed glass or stainless steel collection plates were used in this study. Back-up filters were either Millipore type AAWP 0.8μ or Gelman 0.3μ Type A 142 mm diameter. Millipore filters were routinely used while the Gelman filters were used for special analytical applications.

3. Single Proportional Filter

A total mass emission rate at the sampling zone of the diluted exhaust was obtained by pulling an isokinetic proportional sample at 4 cfm through a single 142 mm filter of the types mentioned above. This technique was found necessary in order to obtain relatively large sample mass for analytical purposes. This sampling system operated in the same zone as the Andersen Samplers.

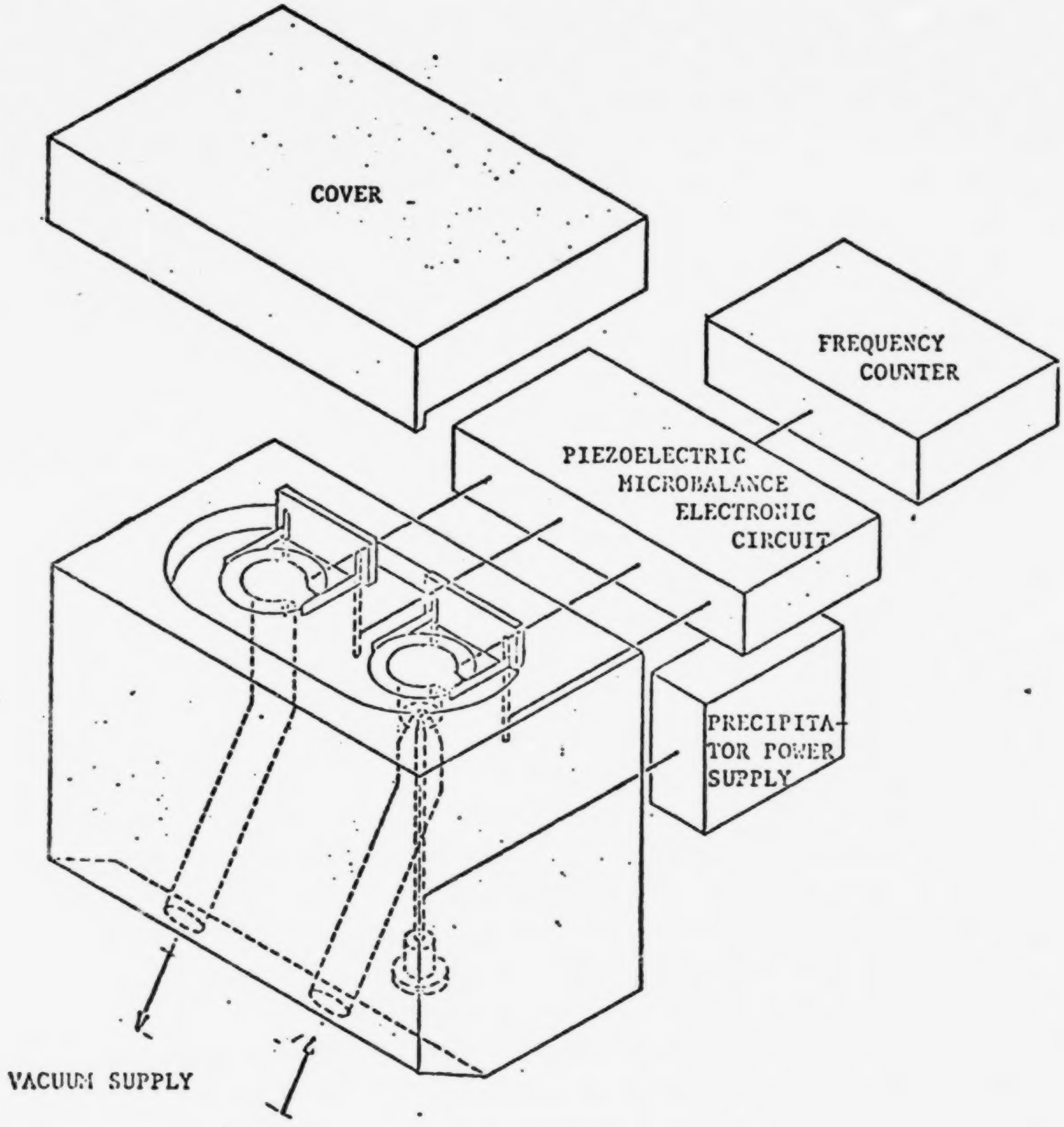
4. Piezoelectric Crystal

All piezoelectric crystal mass monitors are based on the same principle. A piezoelectric crystal, such as quartz, is placed in an oscillating electric field, the latter oscillating at a frequency close to the crystal's natural frequency of vibration(3). If small particles attach themselves to the surface of the crystal, the natural frequency of the crystal decreases. The change in natural frequency is detected and is proportional to the mass of the attached particles. The sensitivity of these devices is exceptional, easily detecting mass changes of tenths of micrograms.

Two commercial versions have been developed utilizing different techniques to collect the particles on the crystal. The instrument developed by Atlantic Research(4) uses impaction as the collection technique. Particles larger than a specified size are accelerated through an orifice and impact on the surface of the crystal which is coated with an adhesive. Particles smaller than the cutoff size follow the air stream past the crystal. Because of the theoretical limitations of this collection technique, particles less than 0.3μ diameter cannot be satisfactorily collected on the crystal with the Atlantic Research instrument. Thermo-Systems, Inc.(5) with funding by EPA have also developed a piezoelectric crystal monitor, which was used in this program. A schematic is shown in Figure 3. This instrument uses a point to plane electrostatic precipitator to deposit the particles onto the crystal. An external vacuum source draws a 1 liter/min sample stream through an intense corona discharge near the needle point negatively charging the particles. The air flow and electric field carry the particles to the surface of the crystal. A second crystal, the one on the left in Figure 3, is used as a reference crystal to correct for environmental changes.

Figure 3

Crystal Monitor


COVER
FREQUENCY COUNTER
PIEZOELECTRIC MICROBALANCE ELECTRONIC CIRCUIT
PRECIPITATOR POWER SUPPLY
VACUUM SUPPLY
AEROSOL IN

5. Beta-Gauge

A prototype Beta-gauge and tape sampler system(6) was also evaluated (Figure 4). The tape sampler collects the particulate sample on a filter and the mass collected on the tape is determined from the Beta gauging technique. With this technique, the tape is placed between a beta source, in this case C^{14}, and a beta radiation detector. A fraction of the radiation from the source passes through the filter tape and the particulate deposit to the detector. The greater the mass of the particulate deposits on the tape, the less is the amount of radiation reaching the detector. After correcting for the mass of the tape medium and the background radiation, the mass loadings on the tape can be calculated.

C. ANALYSIS

Collected exhaust particles have been analyzed for both physical and chemical character. Many analytical techniques have been employed, some of which provide very similar data in the interest of correlating trends observed. This section reviews the basic analytical concepts applied to each of the many test components from fuels to exhaust particles. Detailed descriptions of the specific analytical procedures employed are then presented.

1. Fuels

Each test fuel was analyzed to verify concentrations of additives under study. Additionally, complete physical (distillation, octane numbers, fluorescence indicating analysis [FIA] composition, and Reid vapor pressure [RVP]) and trace metal analysis was determined.

2. Oils

Engine oils were examined for trace metals both before and after test runs. Compliance of physical properties with specifications was verified.

B Gauge & Tape Sampler System

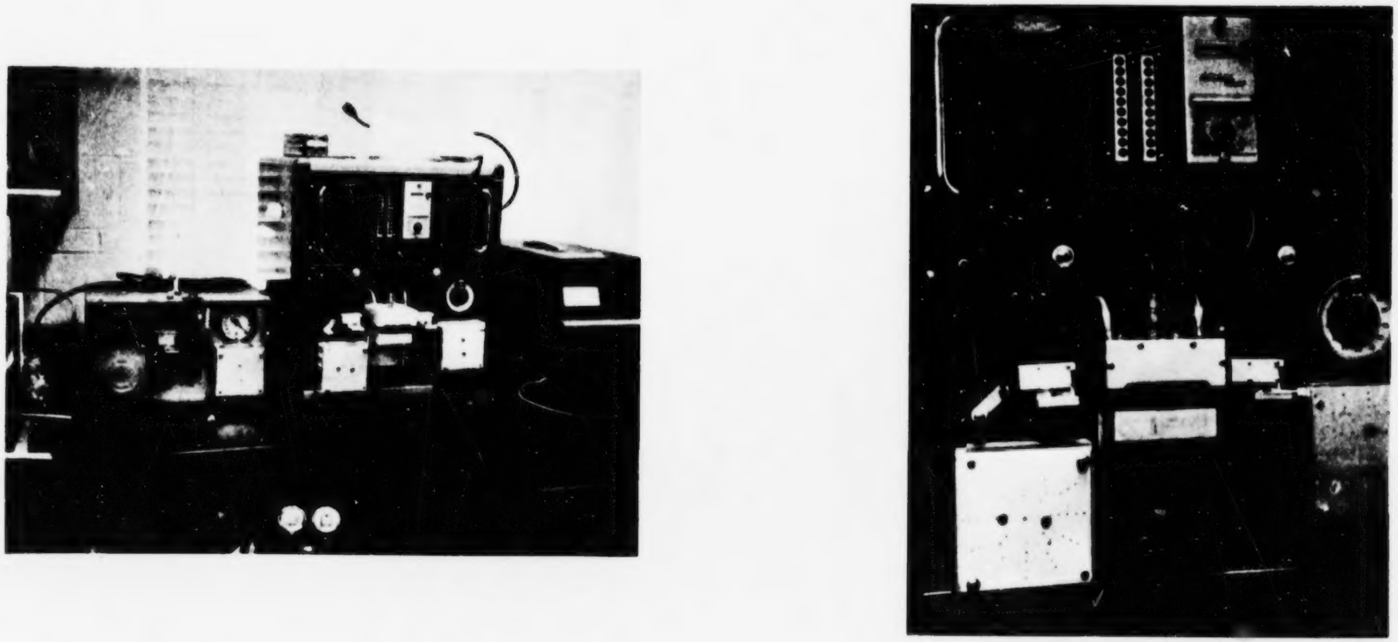


Figure 4

3. Diluent Air

Mass and composition of the filtered diluent air particulate was determined with the engine or vehicle operating in the air pick-up zone as during a test run. This data was necessary to provide a correction factor applicable to the mass emission rates determined during a test run.

4. Exhaust Gases

Engine exhaust gases were analyzed routinely several times during the conditioning sequence and during sampling runs. Schematically, exhaust gas sample points are as shown earlier in Figure 2 (page 20). The engine exhaust gas was analyzed for oxygen, nitrogen, carbon monoxide, carbon dioxide, and total hydrocarbons. The hydrocarbons were broken down into saturates and unsaturates. These analyses were done by gas chromatography, chemical absorption, and a total hydrocarbon analyzer. Data reduction was via an IBM 1800 computer through a Bell Telephone ASR 33 Teletype interface.

a) Analytical Equipment

A Fisher Gas Partitioner was used for the analysis of oxygen, nitrogen, carbon monoxide, and carbon dioxide. The partition column consisted of a 6-foot section containing hexamethyl phosphoramide and a 6-1/2 foot section containing 13x molecular sieves in series.

Total hydrocarbons were obtained from a Beckman Model 109A Total Hydrocarbon Analyzer. The concentration of unsaturated hydrocarbons was determined by passing the sample through an absorption tube (1/2" x 8") filled with 30-60 mesh pink Chromosorb impregnated with 50 percent mercuric perchlorate.

The output of the gas chromatograph was coupled with a Hewlett-Packard Model 3370A Digital Intergrator which has an ASCII coded output to drive an ASR 33 Teletype and punch paper tape.

b) Sampling

A Neptune Dyna-Pump was used to pull the sample from the exhaust pipe sampling point through 1/4" OD stainless steel tubing and transfer it to the total hydrocarbon analyzer and the gas sampling valve of the gas chromatograph through 1/8" OD stainless steel tubing. A manifold system was provided to allow the operator to calibrate the equipment with the appropriate standards.

c) Standardization

A gas mixture containing known concentrations of oxygen, nitrogen, argon, carbon monoxide, carbon dioxide, and n-hexane was used as a reference standard for the total hydrocarbon analyzer and the Fisher Gas Partitioner.

d) Operation

The operator typed the proper computer code and program number on the teletypewriter, injected the reference standard, and pressed the integrator start button. As the peaks emerged, the time and area information was encoded and stored on punched paper tape. Each succeeding exhaust gas was identified along with the total hydrocarbon level, and run in the same manner as the standard. When the series was finished, the punched tape was sent to the computer by teletype over regular telephone lines.

e) Data Reduction

A typical output format for the gas analysis is shown in Figure 5. Identification of the components in the standard was based upon each peak size in descending order. Estimated retention time was the updated time of each peak in the standard. Retention time windows are 4 seconds plus 2 percent of the retention time. Actual percent is a direct ratio of the area counts in the unknown sample to the area counts in the standard times the volume percent in the standard. The total percent actual will normally be 97-98 percent since water is removed from the saturated sample after the sampling valve.

A correction for the unresolved argon in oxygen was made based upon response factors and the amount of argon found in a number of exhaust gas samples by mass spectroscopy.

The actual percent was normalized to 100 percent in the next column on a moisture free basis, and an Exhaust Gas Analysis report was issued (Figure 5). The air-to-fuel ratio was calculated from this analysis, the total hydrocarbon content, and the percent carbon in the fuel.

b. Oxides of Nitrogen

1) Equipment

Beckman Ultraviolet Analyzer
Beckman Infrared Analyzer
Recorder - Texas Instrument Company

The above pieces of equipment were in a single, self-contained unit built by Scotts Research Labs Inc., San Bernardino, California.

Figure 5

```
G. C. ANALYSIS - TECHNICAL DATA -                 10-16-70
GØV RUN 23 ØCT 16
CYCLE 2 72.9 HØURS
HC 620.

 PEAK     TIME          PCT. VØL.         CØMPØUND
  NØ.  ACT.   EST.   ACTUAL    NØRM.   IDENTIFICATIØN


   1     22.    21.    0.000     0.000  CØMPØSITE
   2     59.    59.   12.003    12.366  CARBØN DIØXIDE
   3     83.    83.    1.493     1.530  ØXYGEN
                       0.900     0.927  ARGØN
   4    104.   107.   81.038    83.492  NITRØGEN
   5    187.   188.    1.626     1.675  CARBØN MØNØXIDE
                     -------   -------
                      97.060   100.000  TØTALS
                       2.940            BALANCE BY DIFFERENCE
                       2.940            TØTAL CØNTAMINATIØN LEVEL

------------------------------------------------------------
------------------------------------------------------------

        EXHAUST GAS ANALYSIS          10-16-70

GØV RUN 23 ØCT 16
CYCLE 2 72.9 HØURS
HC 620.

 TIME  PERCENT  IDENTIFICATIØN

  83.      0.9  ARGØN
 107.     83.5  NITRØGEN
  83.      1.5  ØXYGEN
 188.      1.68 CARBØN MØNØXIDE
  59.     12.4  CARBØN DIØXIDE
         -----
         100.0  TØTAL

FRACTIØN CARBØN IN FUEL 0.8625

TØTAL HYDRØCARBØN CØNTENT  620. PPM.

AIR/FUEL RATIØ 14.8
```

2) Calibrating Gases

Nitric oxide (3545 ppm in nitrogen)
Nitrogen dioxide (862 ppm in nitrogen)

These standard gases were purchased from Scotts Research Labs, Inc.

Nitrogen was used as zero calibrating gas.

3) Procedure

Before making NO, NO_2 measurements, the paper filters (Whatman #3) to each analyzer were changed and the Drierite dryer in the exhaust sample line was replaced. Both analyzers were standardized using the appropriate calibrating gas at a constant flow. The zero standardizing was done using nitrogen as the calibrating gas and using the same flow rate.

After the instrument was standardized, the exhaust gas was passed through the analyzer using the same flow rate as in the standardization step. The NO, NO_2 values were recorded by the dual pen Servo-riter recorder. Figure 2 indicates the source of the exhaust gas sample.

5. Combustion Chamber Deposits

Combustion chamber deposits were carefully removed from valve faces, heads, and piston tops; weighed, and analyzed for major elements and, in some cases, for trace metals.

6. Exhaust Particles

The collection and classification techniques employed allow the calculation of mass emission rates in grams/mile of exhaust particulate. Additionally, cumulative mass distribution data can be calculated. Several collection methods were used, all of which allowed determination of mass emission rates but not cumulative profiles. Additionally, a fairly complex analytical scheme was used to determine chemical composition, trace metals, organic fractionation, crystalline species, NH_3, HCl, H_2O, major elements, and physical character.

D. ANALYTICAL METHODS

1. Optical Microscopy

Optical microscopy was used to provide two basic evaluations of collected particles. First, low magnification documentation of particle character and distribution on collection surfaces and devices (electron microscope grids, etc.) was obtained and, second, documentation of particle size, character, and crystalline morphology at 400x under polarized light. Although several crystalline species were identified by X-ray diffraction, it was not been possible to reliably identify these particles by polarized light alone because of the similar morphology of the different crystalline species.

2. Transmission Electron Microscopy (TEM)

The transmission electron microscope (TEM) was used to characterize and photographically document those exhaust particles which are smaller than one micron and to obtain crystallographic analysis of them by means of electron diffraction. Sampling for this work was done by attaching transmission electron microscope grids, which had been previously given a carbon reinforced collodion substrate, directly onto the Andersen Sampler collection plates and on the Millipore filter following the Sampler. After sampling, the grids were removed and stored in a desiccator to await analysis.

The TEM used was the Phillips EM300 where standard instrumental operating conditions were employed, including a 100 kV operating potential to give the best penetration of the electron dense particles. The particles under consideration here were those ranging in size from 100 to 1000 Å. Photomicrographic documentation was carried out recording similarities and differences as these were observed.

3. Scanning Electron Microscopy (SEM) and X-ray Fluorescence

The Scanning Electron Microscope (SEM) was used to identify (X-ray spectrometer) the collected exhaust particles from the Andersen Sampler and the Millipore backup filter.

a. Instrumentation

Cambridge Stereoscan Mark 2A
Ortec Non-dispersive X-ray Detector
Nuclear Data Analyzer
Varian Vacuum Evaporator
Kinney Vacuum Evaporator

b. Work Outline

1) Particle characterization (SEM) on plates of Andersen Sampler
2) Particle identification (X-ray).
3) Single element X-ray scan.
4) X-ray spectra on impingement area of Andersen plates and spectra on backup filter.

c. Techniques and Methods

1) Substrates for sample collection: The most satisfactory substrates for photomicrography were micro cover glasses, while where X-ray analysis was employed, ultra pure carbon strips proved best. Silica interference from micro cover glasses, halogens in epoxy, and thermal instability in mylar film reduced the desirability for using these materials as substrates where X-ray analysis was to be carried out.

2) Storage and sample preparation: All samples were maintained in a dry atmosphere from collection to

examination. Both the glass cover slip and the carbon strip substratum were attached to SEM sample stubs with conducting silver paint. Samples for SEM characterization were made conductive with a thin layer (∼200 Å) of gold or gold-palladium evaporated. Graphite carbon was sputtered on the samples used for X-ray diffraction.

3) Normal operation for the Stereoscan:
   a) Gun potential - 20 to 30 kV (depending on sample degradation and resolution needed).
   b) Vacuum - $\sim 10^{-4}$ Torr.
   c) Sample angle - 20°
   d) Working distance - 11 mm
   e) Polaroid P/N Type 55 film with 100 sec exposure

4) Normal operations for X-ray Spectrometer (warranted 215 ev FWHM resolution):
   a) Gun potential - 30 kV
   b) 1024 channel - Series 2100 Nuclear Data Multichannel Analyzer
   c) Collection time - 200 sec
   d) Count rate - ∼60 c.p.s.
   e) Spectra recorded on Moseley 7035B X-Y Recorder
   f) Single channel recording
   g) Polaroid P/N Type 55 film
      400 sec or 800 sec exposure depending on concentration

d. Analysis

1) Particle characterization and photomicrographical documentation was done with the scanning electron microscope employing standard operational procedures.

2) Particle identification involved elemental analysis using the X-ray spectrometer on the scanning electron microscope. This included, for multiple particles, full

spectrum elemental scan, and single element scan. Spot scans were carried out on single particles or in specific regions of particles.

4. X-ray Diffraction

Crystalline components in the collected exhaust particles were determined using a 143.6 mm diameter DeBye-Scherrer powder camera with Cu or Fe radiation and a 114.6 mm diameter Guinier-type focusing powder camera with Cu radiation. Diffraction pattern analysis was conducted using the published ASTM Powder Diffraction Standards and our own file of 12,000 standard patterns. The lower limit for detection of a component in a mixture is generally about 5 percent.

5. Mass Spectrometry

Mass spectrometry was used in this project for the semi-quantitative and qualitative comparison of the levels of NH_3, H_2O, HCl, and organics associated with auto exhaust particulates. Different mass spectrometric techniques were tried and their advantages and disadvantages evaluated.

The mass spectra were obtained at 70 ev using a standard 90 degree magnetic sector mass spectrometer. The sample was scraped from the trays of the Andersen Sampler, weighed and devolatilized in a 500 cc reservoir. The vapors were introduced into the ion source of the mass spectrometer through a 2 mil diameter molecular leak while the inlet system was held at 200°C. In an attempt to avoid changes in composition during sampling, the scans were delayed one minute to assure complete volatilization of organics. Both the masses and the intensities of peaks were digitized automatically during scanning of the mass spectrum. A low energy ($\sim$10 ev) mass spectrum of one sample showed the presence of intense peaks at m/e=17, 18 and 36 which could be due to NH_3, H_2O, and HCl. These tentative identifications were extended to other samples.

Assuming that the average instrumental sensitivity for the components in the sample remained approximately constant between samples, the following quantities were calculated as a measure of the relative amounts of NH_3, H_2O, HCl and organics respectively.

$$\left[\frac{I_{17} - 0.21\ I_{18}}{W \times S_t}\right] NH_3, \qquad \left[\frac{I_{18}}{W \times S_t}\right] H_2O$$

$$\left[\frac{I_{36}}{W \times S_t}\right] \text{HCl and} \quad \left[\frac{\sum_{i = 40}^{200} I_i}{W \times S_t}\right] \quad \text{Organics}$$

where I_i is the intensity of the peaks at m/e = i, W the weight in mg of sample loaded, and S_t the toluene sensitivity of the mass spectrometer on the day when the samples were run.

The term $0.21\ I_{18}$ in the case of NH_3 was introduced to correct for the contribution of the fragment ion HO^+ from H_2O to the intensity of the peak at m/e = 17. The mass spectral profile of organics in the auto exhaust particulates was plotted using a B-5500 computer by connecting the mass to charge peak tops after the intensities of the peaks had been normalized by the computer according to the following formula:

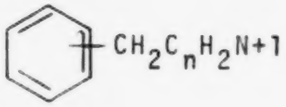
$$\frac{I_i}{\sum_{j = 25}^{250} I_j}$$

$$j \neq 28,\ 32,\ 44,\ 36,\ 38$$

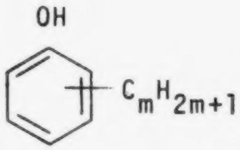
Plots were made of the data for those spectra with enough intensity to be judged significant. The plotted profiles allow one to make a direct comparison of the relative changes in organic composition for the samples obtained at different engine conditions.

The direct probe sample introduction technique was also used in the characterization of the particulates. This technique allows the sample to be heated up to 600°C in a miniature oven located a few millimeters away from the electron beam in the mass spectrometer. The mass spectra were taken at different temperatures of the oven and show the presence of PbClBr, $PbBr_2$, and organic components giving peaks at m/e = 43, 55, 57, 69, 71, et al. However, the technique did not allow one to observe the quantitative differences between samples.

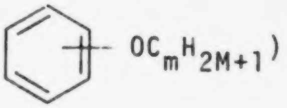
A combination technique of direct probe and field ionization mass spectrometry was also tried. Field ionization mass spectrometry is a technique for ionizing molecules with a high electric field in the order of 0.1v/Å. This is a much milder means of ionization than electron impact. Hence, the fragmentation of a molecular ion is very much reduced in the field ionization mass spectrum and thus the spectral features are simplified. The field ionization mass spectra of only one sample were obtained using a CH4B mass spectrometer. These were weak and complex. However, peaks 14 masses apart are clearly shown in some of the spectra. Two series of peaks were observed: a) m/e = 92 + 14xn, where n = 0-6 or higher, b) m/e = 94 + 14xm, where m = 0-4 or higher, which might be due to the molecular ions of:



and



(or



respectively.

High resolution mass spectrometry was also used in this study to find the accurate masses of the ions observed in the mass spectrum within an accuracy of 5 millimass units. The accurate masses were used for the calculation of the elementary compositions of the ions which should reflect the composition of the sample to some extent. The high resolution mass spectrum was recorded on a photo plate by using a CEC 110B high resolution mass spectrometer. The data were processed with use of a Grand-Datex photo plate reader and a B-5500 computer. It was found that the data obtained were extremely complex and difficult to interpret. However, the hydrocarbon ions were clearly shown in the high resolution mass spectrometric data.

In an attempt to determine the applicability of a small mass spectrometer to direct monitoring of the engine exhaust components and to follow the compositions changes in the exhausts at different engine conditions, a portable cycloidal mass spectrometer was used on line. Gaseous components in the exhaust manifold and in the exhaust pipe after the muffler were sampled. The exhaust sample was introduced into the mass spectrometer through a needle valve with the high pressure end packed with quartz wool to avoid plugging of the valve by the combustion particles in the exhaust stream. Because of the high concentration of H_2O, air, CO, and CO_2 in the exhaust, the mass spectral peaks detected were normalized according to $I_i/\Sigma_{i>54}I$, where I_i is the intensity of the peak at mass i. The normalized mass spectral patterns were plotted employing an IBM 1130 computer by connecting the tops of the normalized peaks at the adjacent masses with a straight line for convenient comparisons between spectra.

For the samples trapped on the glass fiber filter papers, it was extremely difficult, if not impossible, to remove the trapped samples from the filter papers and to obtain their mass spectra in the previously described ways. A special technique was therefore required. Since the filter papers used always absorb moisture, a background spectrum of ∿3 mg of water in a 500 cc reservoir at 200°C was obtained before the samples spectrum. The sample spectra were corrected for peaks shown in the water background which were due to the compounds desorbed from the walls of the spectrometer by the water. The reservoir was then disconnected from the spectrometer and flushed with argon. The filter paper was cut into small pieces and packed on the bottom of the reservoir which was then connected to the spectrometer. The reservoir was chilled with liquid nitrogen for two minutes, pumped to a desired vacuum and then heated to 200°C in about three minutes. The mass spectrum was scanned one minute after the leak valve to the spectrometer had been opened. The mass spectral pattern was then calculated and plotted in the usual manner. No significant peaks, except those due to water, were detected for the unused clean filter paper.

6. High Resolution Mass Spectrometric Analysis

High resolution mass spectra of dilution tube and Andersen samples from run No. 27 (Type A fuel commercial 3 cc TEL) were obtained using a direct introduction probe system and recording spectra as a function of increasing probe temperature and amount of sample evolved. The spectra were recorded on photographic plates and these data were reduced using Shell Oil Company HIRES programs. The sample was introduced at room temperature and allowed to warm up to the ion source temperature by radiation. When no more sample evolved, the sample was removed and placed immediately in the heated probe and spectra were continuously recorded as the probe temperature increased to approximately 400°C. The recording period for each spector was controlled as a function of the integrated ion current. The resulting information was combined after data processing to give a single composite spectrum for each sample. The spectra were recorded on the Ilford Q-2 type plate.

7. Neutron Activation

This method is applicable to the determination of total chlorine and bromine in samples containing 100 to 20,000 μg of chlorine and 1-10,000 μg of bromine. Both bromine and chlorine can be quantitatively and nondestructively determined in the same sample by taking advantage of the large difference in gamma ray energy between the isotopes of bromine and of chlorine.

To further eliminate any possible interference, one can measure the chlorine gamma radiation through a lead absorber which will reduce the bromine radiation to a much larger extent than the chlorine radiation.

Interferences

High levels of sodium may cause a change in sensitivity limits but would not normally prevent analysis. Manganese would also interfere, but is easily detected and if found, the samples can be measured with the high resolution detector with some loss in sensitivity.

Apparatus

a) Automatic sample changer-gamma spectrometer, Nuclear Model 1085 using a 3-inch well NaI(Tl) crystal
b) A solid 3" NaI(Tl) detector with input to sample changer
c) Ionization chamber, 1-2500 mr/hr range
d) TRIGA reactor with maximum flux in the lazy susan of 5×10^{11} neutrons/cm^2/sec
e) Computer-teletype hook-up for calculations
f) Lead "pig" with wall thickness 1/2" and hole diameter of 0.662"
g) Ge(Li) detector and Nuclear Data Model 2200 multichannel analyzer

Reagents

a) Chloride standard solution of 1 mg/ml. Weigh out 0.7546 g NH_4Cl and dilute to 500 ml.

b) Bromide standard solution 1 mg/ml. Weigh out 0.6129 g NH_4Br and dilute to 500 ml.

c) Sodium standard solution 1 mg/ml. Weigh out 1.479 g HCOONa and dilute to 500 ml.

Procedure

a) Sample Preparation - Samples were received in 2 dram polyethylene vials and were heat sealed for irradiation. Standard solutions of chloride, bromide, and sodium were placed in 2 dram polyethylene vials at the same height as the samples and the vials were heat sealed.

b) Irradiation - Samples and standards were initially irradiated at a neutron flux of 5×10^{10} neutrons/cm^2/sec (nv) for 10 minutes. The flux could be increased by a factor of 10 to 5×10^{11} if the initial irradiation produced too little radioactivity. In such a case, one would need standards at a ten-fold dilution.

c) Counting for Chlorine - A 1 ml aliquote of each standard was transferred into a clean 2 dram polyethylene vial and diluted to the volume of the samples. Several types of counting systems may be used depending on the radiation being emitted from the sample. With only chlorine, bromine and sodium present in the sample, the sample should be counted by the 3-inch solid detector (item b under Apparatus) through the lead "pig" (item f under Apparatus) if large amounts of bromine are present. Because of the variation of absorption coefficient with energy of gamma rays passing through lead, this permits a much greater reduction in bromine gamma rays than chloride gamma rays and reduces the interference from bromine.

In this case the output of the 3-inch detector is used as an input to the amplifiers of the sample changer. One of the single channel analyzers in this instrument is sent to cover the chlorine-38 gamma ray at 2.16 Mev, the secone single channel analyzer is set to cover the sodium-24 gamma ray at 2.75 Mev.

Two or four minute counts can be taken at the discretion of the analyst.

The sample changer was used as a timing device and to record the counts observed, but the samples were changed by hand each time the printer prints a set of data. All samples and standards were counted twice.

If manganese is found to be present in the samples, the samples must be counted with the Ge(Li) detector. The information which is stored in the memory of the analyzer must be read out on paper tape after each measurement. The peak areas are then integrated by summing the counts in each channel over the region of interest. Samples which show very low amounts of radioactivity can be counted in the well type NaI(Tl) detector in the sample changer. Again, the single channel analyzers were set to cover the chlorine and sodium gamma rays.

Bromine standards were counted any time a NaI(Tl) detector was used so that the contribution to the chlorine can be subtracted once the amount of bromine is determined.

d) Counting Bromine - After the chlorine and sodium have decayed away, the bromine-82 can be measured either with the solid NaI(Tl) detector or with the well detector depending on the radiation intensities. A single channel analyzer was set to cover the bromine-82 gamma ray region from 0.554-0.777 Mev.

Calculations for Use of NaI(Tl) Detector

Calculations were made for bromine first.

a) $$\frac{(\text{Std bromine counts-background}) \times \text{decay corr.}}{\mu\text{g of Br}} = \frac{\text{counts}}{\mu\text{g Br}} = B$$

$$\frac{(\text{counts for sample-background}) \times \text{decay corr.}}{B} = \mu\text{g bromine}$$

Calculations for chlorine proceeded as follows:
The bromine contribution to the chlorine measurement was subtracted as follows:

μg Br in sample x count in Br std. during Cl measurement =
Bromine count to be subtracted from chlorine count (A)

Chlorine count - A = true chlorine count

If sodium were present then the bromine conbribution to the sodium must also be subtracted.

Dual channel cross-interference calculations for the sodium contribution to the chlorine were made by computer.

Since there was a very broad range in the amounts of bromine and chlorine in the samples investigated, it was necessary to be thoroughly familiar with all possible counting techniques.

Immediate decisions had to be made on the proper counting device to be used because of the short half life of chlorine-38 (37.3 min.).

Since the whole procedure is nondestructive, samples could be returned after a sufficient decay period for the determination of lead by other techniques(7).

8. Atomic Absorption

a. Method for Lead Determination

Following nitric acid digestion, particulate samples were washed into 50-ml volumetric flasks and diluted to mark. This normally put the concentration of lead in the flasks between 20 and 200 μg Pb/ml. If the concentration was higher than 200 μg Pb/ml, the sample required redilution. The samples were analyzed on an atomic absorption spectrophotometer (Perkin-Elmer Model 303) using a hollow cathode lamp with a lead cathode filament. Operating conditions were as follows: 10 milliamps tube current, light path slit opening - 4, ultraviolet light range, acetylene-air oxidizing flame, one-slot burner head, wavelength - 2170 angstroms. The sample solution is aspirated into the flame where lead atoms present absorb the light from the lead cathode filament. The amount of absorbed light is proportional to the concentration of lead. The samples were analyzed in conjunction with the following series of lead standards: 10, 20, 40, 60, 80, 100, 150, and 200 μg Pb/ml. The concentration of the standards was plotted versus their absorbance values giving a standard curve. With the absorbance values for the samples and the standard curve, it was possible to determine the concentration of lead in the samples. The sensitivity for the lead determination in an air-acetylene flame is about 0.25 μg Pb/ml at 1 percent absorption. The detection limit is 0.1 μg Pb/ml.

b. Determination of Lead and Iron in Engine Combustion Chamber Deposits

These samples were thoroughly ground in a mortar prior to analysis to obtain uniform samples. The ground sample was dissolved in nitric acid and lead determined by atomic absorption. A portion of the sample solution was also used in the determination of iron. Iron is reduced with hydroxylamine to the ferrous state, and reacted with 1,10-phenanthroline in an acetate buffered solution (pH 5) to form an orange-red complex. Photometric measurements were made using a Beckman DU-2 spectrophotometer. Operating conditions were as follows: sensitivity setting - 2, slit opening - 0.10 mm, wavelength - 510 nm, 40 mm optical cells. The concentration of iron was determined from a standard curve. For a one gram sample diluted to 100 ml, the detection limit is about 1 ppm and the sensitivity ± 1 ppm.

c. Gravimetric Method for Lead Determination in Millipore Filters

Following nitric acid digestion, concentrated sulfuric acid was added to the sample to precipitate lead sulfate. The solution was filtered, and the precipitate dried and weighed to determine the amount of lead percent. In addition, the filtrate was analyzed by atomic absorption for trace amounts of lead. This analysis is included in the total amount of lead reported for the sample.

d. Determination of Lead and Other Metals in Fiberglass Filters

The fiberglass filters cannot be digested completely with nitric acid. They were cooked with concentrated nitric acid for two hours to leach out the metals. The pulp was filtered and washed and the filtrate analyzed by atomic absorption for lead, and by emission spectroscopy for other metals.

9. Emission Spectrometry

a. Principle

Organic matter in the sample is destroyed by wet ashing in sulfuric, nitric and perchloric acids. The resulting solution is taken to dryness and the residue is taken up in a spectroscopic buffer solution containing the internal reference element, palladium. A portion of the solution is dried on pure graphite electrodes. The electrodes thus prepared are excited in an a.c. arc discharge and the spectrum is photographed. The intensity ratios of selected lines are determined photometrically and the concentration of each element is read from an analytical curve relating intensity ratio to concentration.

b. Apparatus

1) Excitation. Excitation is obtained by the use of a 2400 volt a.c. arc discharge - Jarrel-Ash Custom Varisource, or equivalent.

2) Spectrograph - Baird 3 meter grating spectrograph. Reciprocal dispersion is 5.55 A/mm in the first order.

3) Developing equipment - Jarrel-Ash Company. Plates are developed in a thermostatically controlled developing machine, washed and dried over heat in a stream of air.

4) Densitometer. Spectral lines are measured with a non-recording projection type densitometer. Densitometer Comparator, Baird Associates Inc., or equivalent.

5) Calculating equipment. A calculating board is employed to covert densitometer readings to log intensity ratios. Jarrel-Ash Co.

6) Wet ashing equipment. A micro Kjeldahl digestion rack is used for wet ashing the organic solvents.

c. Reagents and Materials

1) Distilled nitric and perchloric acids. Perchloric acid is an intense oxidizing agent. Organic matter should not be heated in perchloric acid unless in the presence of sulfuric or nitric acid.
2) Sodium nitrate, reagent grade ($NaNO_3$).
3) Palladium diamine nitrite, $Pd(NH_3)_2(NO_2)_2$.
4) Water soluble salts of the elements Al, Ca, Cu, Fe, Mg, Mn, Ni, Pb, Sn, and Zn.
5) Electrodes, high purity graphite, 1/4" diameter by 3/4" length. Ultra Carbon Corporation.
6) Photographic plates - Eastman Spectrum Analysis No. 3.
7) Kjeldahl flasks, 10 ml.

d. Calibration

1) 0.2182 gm of palladium diammine nitrite $Pd(NH_3)_2NO_2)_2$ were dissolved in water. 10 ml of concentrated reagent grade nitric acid were added and the mixture diluted to volume with water in a 100 ml volumetric flask. This solution contains 1 mg Pd per ml.

2) A buffer solution was prepared by dissolving 20 gm of sodium nitrate in water. 5.0 ml of the palladium solution above and 7.5 ml of concentrated reagent grade nitric acid were added and the whole diluted to 100 ml.

3) A stock solution containing 0.01% (0.1 mg/ml) each of the elements Al, Ca, Cu, Fe, Mg, Mn, Ni, Pb, Sn, and Zn was prepared. Two aliquots of this solution were diluted ten-fold and one hundred-fold to provide 0.001% and 0.0001% solutions.

4) Standard additions of the impurity elements were made to Kjeldahl flasks as shown in Table 7.

5) 0.5 ml of concentrated reagent grade sulfuric acid was added to the Kjeldahl flasks and the solution evaporated to dryness. After cooling, 1 ml of concentrated nitric acid was added and the mixture was evaporated to dryness again. The residue was taken up in 5 ml of buffer solution, warming, if necessary, to put the salts into solution.

6) The end of the 3/4" graphite electrodes was polished on filter paper and placed in a stainless steel drying tray. A drop of kerosene was placed on the top of each electrode to seal the porosity and the electrode allowed to dry. One pair of electrodes was prepared for each of the standard addition solutions by pipetting 0.03 ml of the solution onto the end of each electrode. The electrodes were dried slowly over micro burners in a gas drying oven and stored in a desiccator until run.

7) The samples were excited in water cooled electrode holders using the following conditions:

(1) Current, 4.0 amps, a.c. arc.
(2) Spectral region, 2150-3550 A.
(3) Slit width, 50μ.
(4) Electrode gap, 2 mm.
(5) Pre-burn period, 10 seconds.
(6) Exposure period, 90 seconds.

8) The emulsion was calibrated by use of a stepped filter or by other recommended methods described in the "Recommended Practice of Photographic Photometry in

Table 7

Concentration	ml. of standard addition impurity solution		
Blank			
0.00001%	0.5 ml.	0.0001%	solution
0.000025%	1.25 ml.	"	"
0.00005%	0.25 ml.	0.001%	"
0.0001%	0.5 ml.	"	"
0.00025%	1.25 ml.	"	"
0.0005%	2.5 ml.	"	"
0.00075%	0.375 ml.	0.01%	"
0.001%	0.5 ml.	"	"
0.0025%	1.25 ml.	"	"
0.005%	2.5 ml.	"	"
0.01 %	5.0	"	"

Table 8

Analytical Line Pairs

Element	Analytical Line A	Internal Standard Line A	Concentration Range %
Al	3092.71	3027.91 Pd	0.000025-0.0010
Ca	3179.33	"	0.00025-0.010
Cu	3273.96	"	0.00001-0.00025
Fe	3021.07	"	0.0001-0.010
Fe	3020.64	"	0.000025-0.0050
Mg	2802.69	"	0.000025-0.0010
Mg	2779.83	"	0.0005-0.010
Mn	2933.06	"	0.0005-0.010
Mn	2794.82	"	0.00001-0.0010
Ni	3414.77	"	0.000025-0.0010
Ni	3037.94	"	0.0005-0.010
Pb	2873.32	"	0.0010-0.010
Pb	2833.07	"	0.00005-0.0050
Sn	3175.02	"	0.00005-0.0050
Sn	2863.33	"	0.00075-0.010
Zn	3345.02	Background	0.0001-0.010

Spectrochemical Analysis" A.S.T.M. Designation: E116, Methods for Emission Spectrochemical Analysis, (1964).

9) The emulsion was processed according to the following conditions:

(1) Developer (D19, 20.5°C), 3 1/2 minutes.
(2) Stop bath (SB-4), 1 minute.
(3) Fixing bath (Kodak Rapid Fixer), 2 minutes.
(4) Washing, 3 minutes.
(5) Drying, in a stream of warm air.

10) The relevant analytical line pairs were selected from Table 8. The relative transmittances of the internal standard line and each analytical line were measured with a densitometer. The transmittance measurements of the analytical line pairs were converted to intensity ratios by the use of an emulsion calibration curve and a calculating board.

11) Analytical curves were constructed by plotting concentration as a function of intensity ratio on log-log graph paper. For best results, the average of at least four determinations recorded on two plates were plotted.

e. Procedure

1) The available sample was weighed directly into a Kjeldahl flask. Sulfuric acid was not used in the wet ash procedure because test samples usually contained a large amount of lead which would form the insoluble sulfate. Wet oxidation was carried out with nitric and perchloric acid only. Extreme caution was exercised in the use of this technique. Concentrated nitric

acid was added dropwise, a few tenths ml at a time, to the hot mixture to aid in oxidation. A few drops of concentrated perchloric acid may be added to the hot solution after most of the free carbon has been destroyed, to hasten complete oxidation. When the solution became water clear, it was evaporated to dryness. After cooling, 0.5 ml of nitric acid was added and the mixture evaporated to dryness. The addition of 0.5 ml of nitric acid was repeated and the solution evaporated to dryness again. The inorganic residue was dissolved in dilute nitric acid and the volume adjusted to a known concentration, usually 10 mg/ml. If the original sample size was below 30 mg, a less concentrated solution was usually made up. Aliquots of this solution were taken to dryness and then the buffer solution (d2) added in an amount to give a dilution factor of 100x. One sample was analyzed by the direct reader while a second was examined photographically. Some samples had to be run at factors larger than 100x in order to get the concentration for some elements to fall within the range of the analytical curves. By varying the sample to buffer ratio any number of concentration or dilution factors could be achieved. A blank of the acids used was carried through in the same manner as the sample.

2) Proceed as in d(6), (7), (8), (9), and (10) of the calibration procedure. Duplicate spectra were recorded for each sample.

f. Calculations

The intensity ratios were converted to concentration by use of the analytical curves.

g. Precision and Accuracy

Representative precision and accuracy of the method are given in Table 9. Each of the twelve samples A_1, A_2, A_3, B_1, B_2, B_3, C_1, C_2, C_3, D_1, D_2, D_3, was analyzed by means of duplicate excitation(8,9).

10. Polarography

The analytical method for the determination of carbonyl compounds in automotive exhaust emissions employed polarographic techniques. Samples for analysis were collected from undiluted exhaust effluent using ice-water cooled cold traps and via a sample probe welded into the engine or vehicle exhaust system. A Princeton Applied Research Model 170 Electrochemistry System was used as the monitoring device. The derivative pulse polarographic mode yielded the best combination of resolution and sensitivity for the classification of carbonyl compounds. A dropping mercury electrode with a Princeton Model 172 Drop Timer was employed as the working electrode.

Hydrazine derivatives (hydrazones) were employed for the determination of the carbonyl compounds, since hydrazones are easier to reduce than the free compounds, thus eliminating many possible interferences.

An acetate buffer of approximately pH 4 (an equimolar mixture of acetic acid and sodium acetate, 0.1M in water) was used to control pH for hydrazone formation and also acted as supporting electrolyte. Hydrazine was added as a 2 percent aqueous solution. In this system formaldehyde gave a peak potential (half-wave potential) of -0.92v vs. a saturated calomel reference electrode. A platinum wire was employed as the auxiliary electrode.

With the above system, it is possible to distinguish between and simultaneously determine aromatic aldehydes, formaldehyde, higher aliphatic aldehydes, and aliphatic ketones as shown in Figure 6.

TABLE 9

Representative Precision and Accuracy

Sample	% Al	% Ca	% Cu	% Fe	% Mg	% Mn	% Ni	% Pb	% Sn	%Zn
A_1	0.000044	0.00043	0.000048	0.00043	0.00049	0.00046	0.00047	0.00056	0.00052	0.00040
	0.000052	0.00050	0.000054	0.00055	0.00052	0.00057	0.00055	0.00059	0.00059	0.00045
A_2	0.000045	0.00043	0.000046	0.00044	0.00047	0.00051	0.00045	0.00050	0.00053	0.00054
	0.000052	0.00037	0.000047	0.00043	0.00050	0.00050	0.00051	0.00051	0.00050	0.00040
A_3	0.00004	0.00043	0.000050	0.00046	0.00053	0.00049	0.00047	0.00052	0.00050	0.00052
	0.000052	0.00050	0.000048	0.00046	0.00049	0.00046	0.00048	0.00053	0.00046	0.00042
B_1	0.00012	0.00105	0.00012	0.0010	0.00105	0.0010	0.0010	0.00105	0.0011	0.00094
	0.000097	0.00093	0.00010	0.00094	0.00095	0.0012	0.00096	0.00098	0.00094	0.0012
B_2	0.000097	0.00086	0.000099	0.00090	0.00092	0.0011	0.0010	0.0010	0.00105	0.00125
	0.000094	0.00068	0.000095	0.00105	0.00091	0.00066	0.00105	0.00105	0.00105	0.0010
B_3	0.000082	0.00085	0.000095	0.0010	0.0010	0.00086	0.0010	0.0010	0.00099	0.00096
	0.00011	0.00074	0.000096	0.0010	0.00090	0.00092	0.00105	0.0010	0.0010	0.00115
C_1	0.00028	0.0023	0.00023	0.0025	0.0023	0.00265	0.00245	0.00235	0.00255	0.0014
	0.00030	0.0018	0.00028	0.0030	0.0023	0.00195	0.00265	0.00255	0.0027	0.00215
C_2	0.00020	0.00225	0.00023	0.0023	0.0023	0.00265	0.0023	0.00245	0.00215	0.00225
	0.00023	0.00265	0.00025	0.00235	0.0024	0.00275	0.00245	0.0026	0.0023	0.0030
C_3	0.00024	0.0025	0.00026	0.00275	0.0023	0.00245	0.0026	0.0025	0.0025	0.0030
	0.00028	0.00275	0.00028	0.00285	0.0024	0.0025	0.00255	0.00245	0.00265	0.0020
D_1	0.00074	0.0070	--	0.0065	0.0057	0.0059	0.0065	0.0056	0.0064	0.0058
	0.00064	0.0054	--	0.0063	0.0051	0.0058	0.0058	0.0045	0.0059	0.0050
D_2	0.00059	0.0049	--	0.0057	0.0048	0.0045	0.0056	0.0045	0.0053	0.0050
	0.00063	0.0057	--	0.0059	0.0047	0.0048	0.0057	0.0048	0.0057	0.0060
D_3	0.00059	0.0048	--	0.0050	0.0045	0.0047	0.0050	0.0043	0.0054	0.0037
	0.00053	0.0060	--	0.0055	0.0055	0.0054	0.0055	0.0049	0.0049	0.0041

A_1, A_2, and A_3 contain 0.00005% of Al and Cu, and 0.0005% of each other element. B_1, B_2, and B_3 contain 0.0001% of Al and Cu, and 0.0010% of each other element. C_1, C_2, and C_3 contain 0.00025% of Al and Cu and 0.0025% of each other element. D_1, D_2 and D_3 contain 0.0005% of Al and Cu and 0.0050% of each other element.

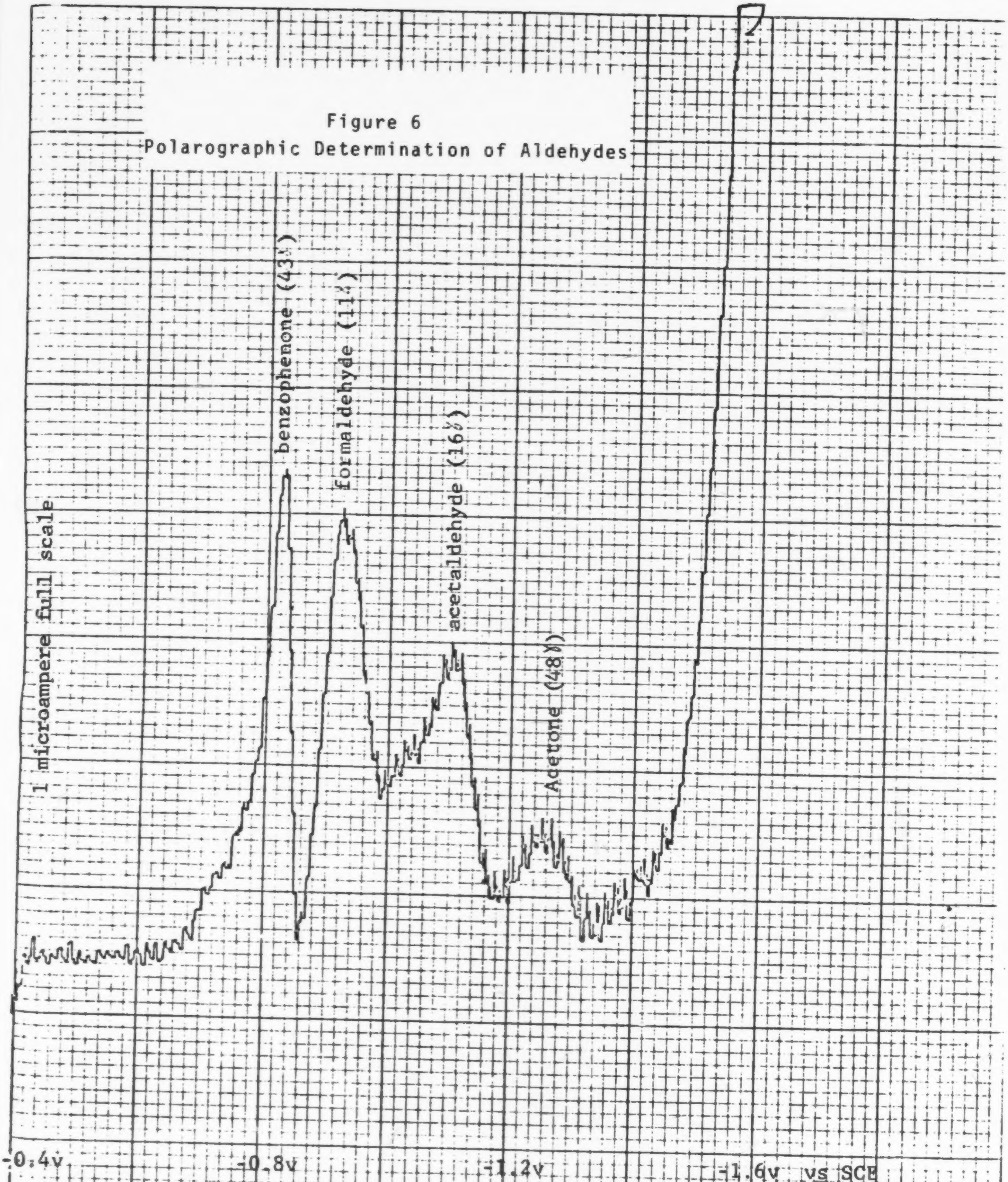


Figure 6
Polarographic Determination of Aldehydes

Since aromatic ketones, e.g. benzophenone, give polarographic response in pH 4 buffer without hydrazine, it is also possible to detect aromatic ketones. Lead and zinc could also be determined from the samples under these conditions.

Since formaldehyde was the main carbonyl component of the condensate samples, all results were calibrated against and reported as formaldehyde. The upper curve in Figure 7 shows an actual sample without hydrazine present and demonstrates the lack of interference in the carbonyl region. The lower curve shows the same sample after the addition of hydrazine. Figure 8 shows the same solution after the addition of a formaldehyde standard. These two figures clearly establish the presence of formaldehyde in the exhaust samples.

Experimental

The absorptivity at 255 nm of benzene soluble particulate residues can be used as a measure of aromaticity. As shown in Figure 9, $PbBr_2$ has an absorptivity of 16.6 at 255 nm. Thus the presence of lead compounds can alter the absorptivity and produce an erroneous measure of aromaticity. Measurement of the absorptivity at 300 rather than 255 nm minimizes the interference of lead compounds in measuring aromaticity.

Lead can be polarographically determined as Pb^{++} in pH 4 acetate buffer. The peak potential is -0.42v vs. SCE. Figure 10 demonstrates the presence of lead in an actual run and Figure 11 shows the recovery of added Pb (added as $PbCl_2$).

A description for the polarographic examination of these samples follows.

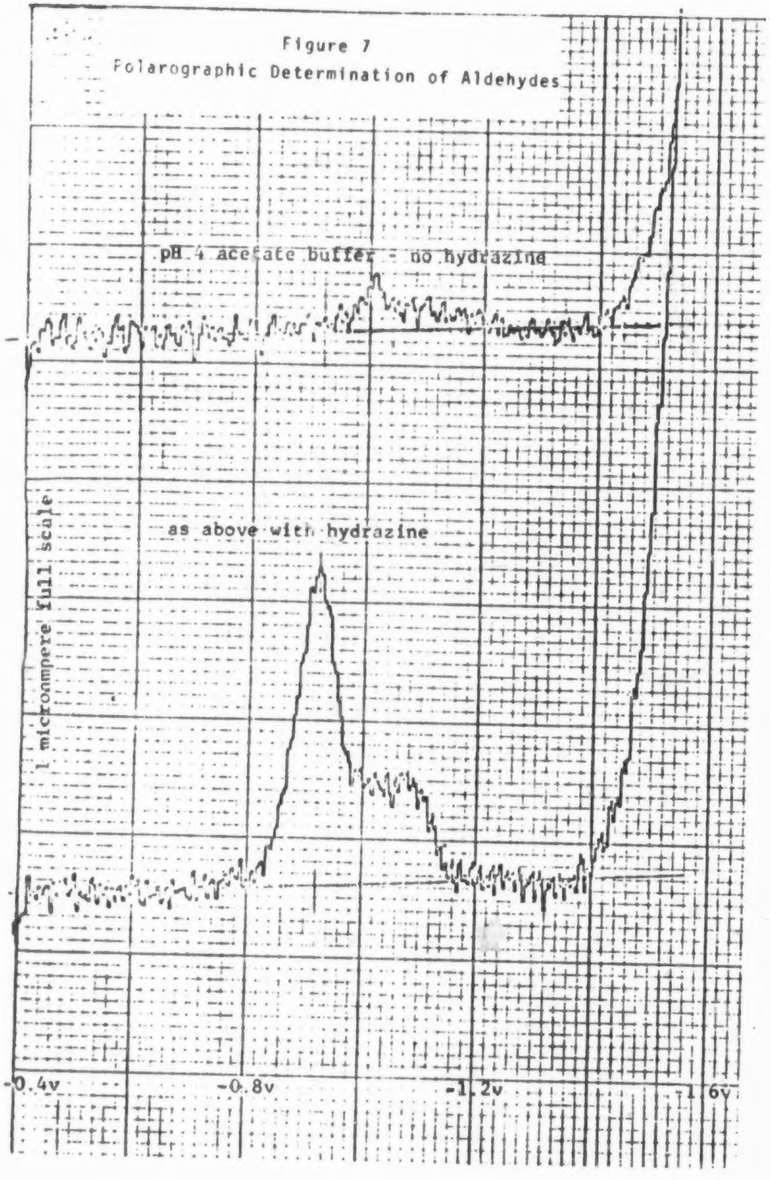


Figure 7
Polarographic Determination of Aldehydes

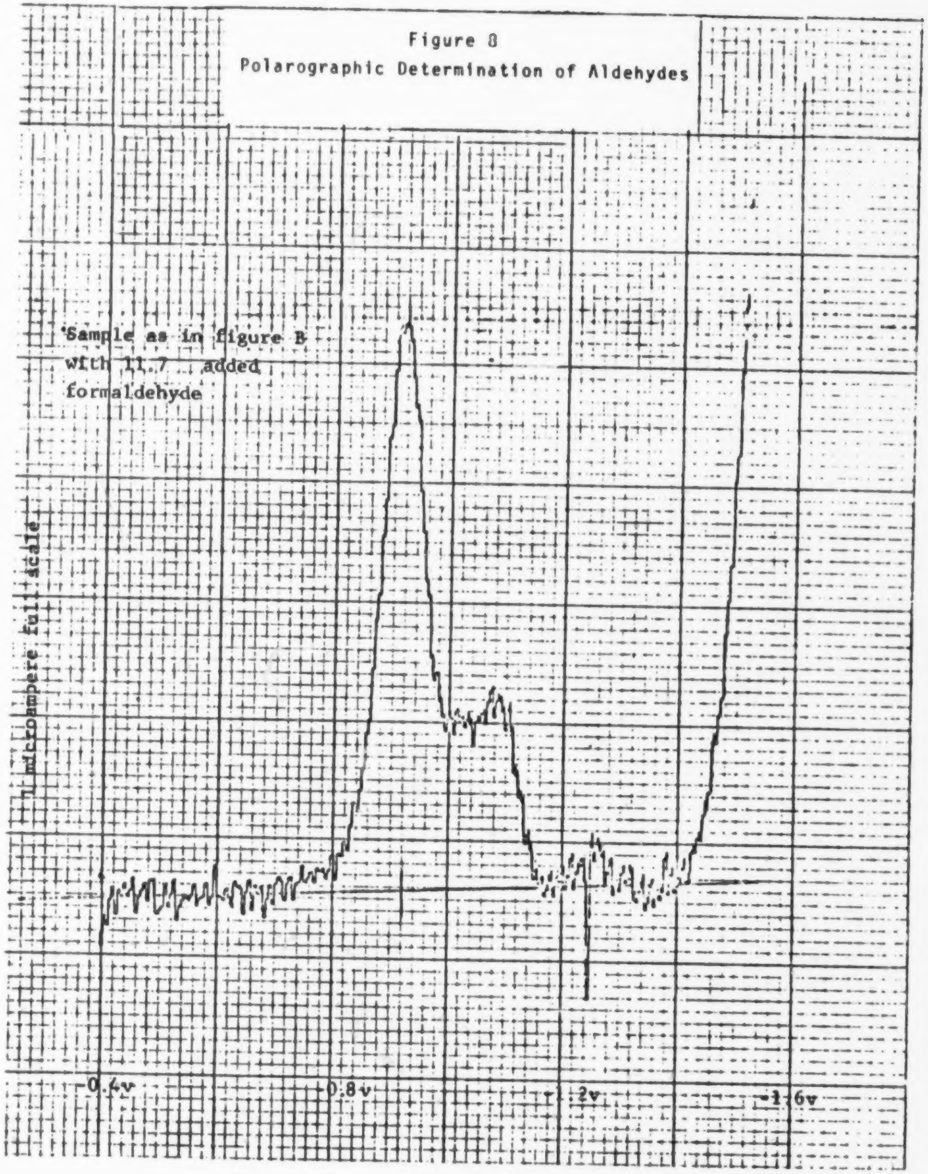


Figure 8
Polarographic Determination of Aldehydes

Figure 9

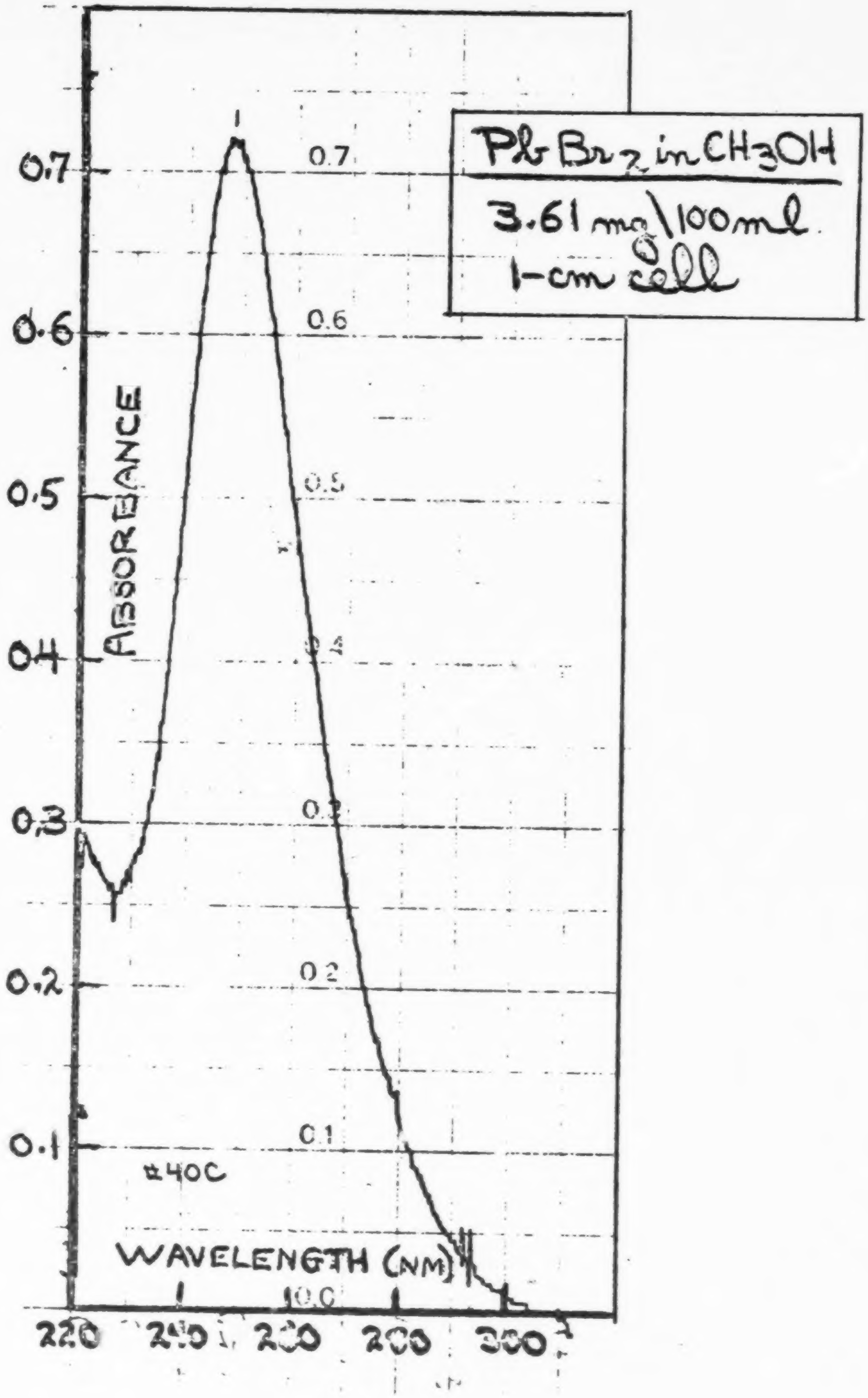
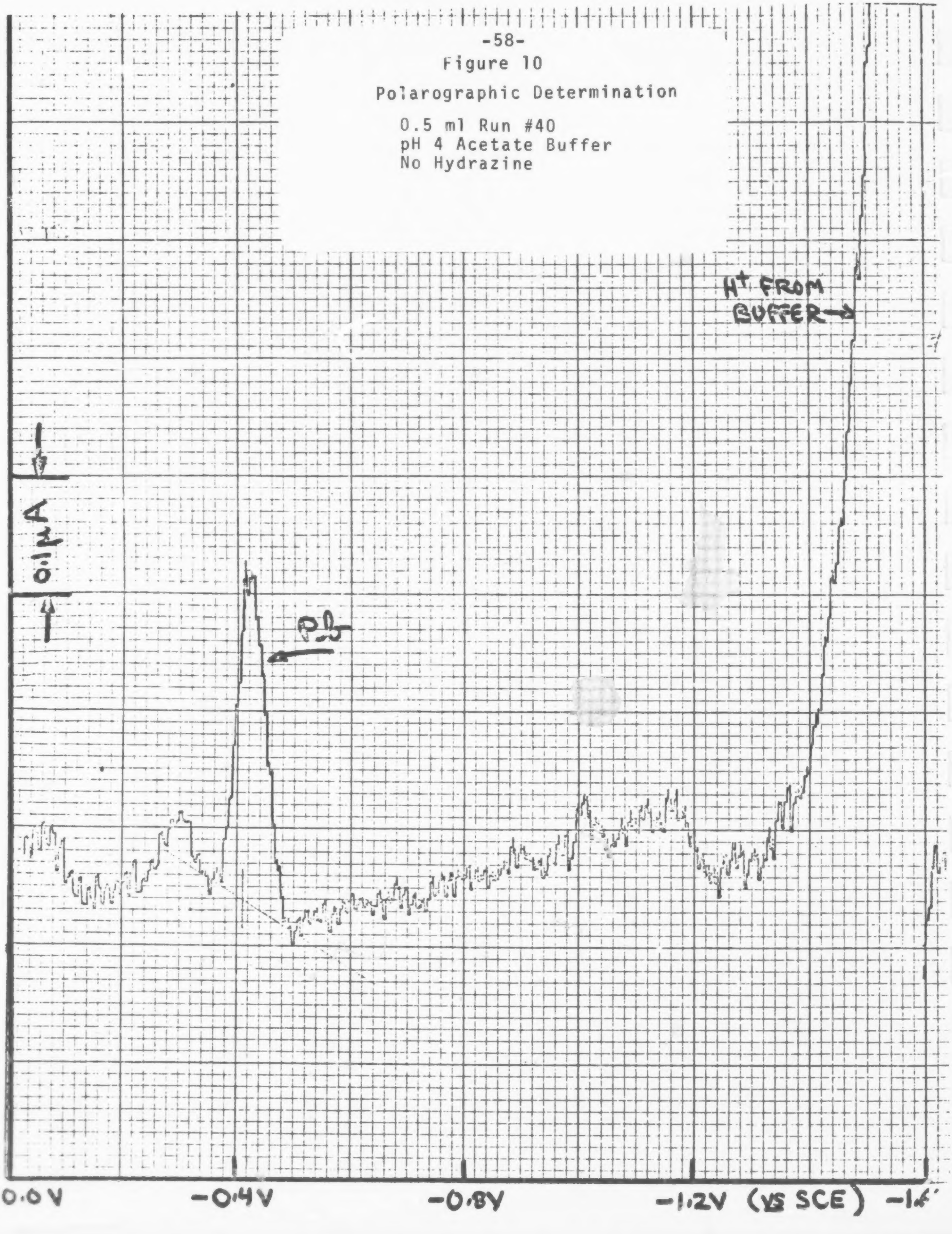

PbBr$_2$ in CH$_3$OH
3.61 mg\100ml
1-cm cell
ABSORBANCE
0.7
0.6
0.5
0.4
0.3
0.2
0.1
#40C
WAVELENGTH (NM)
220
240
260
280
300

Figure 10

Polarographic Determination

0.5 ml Run #40
pH 4 Acetate Buffer
No Hydrazine



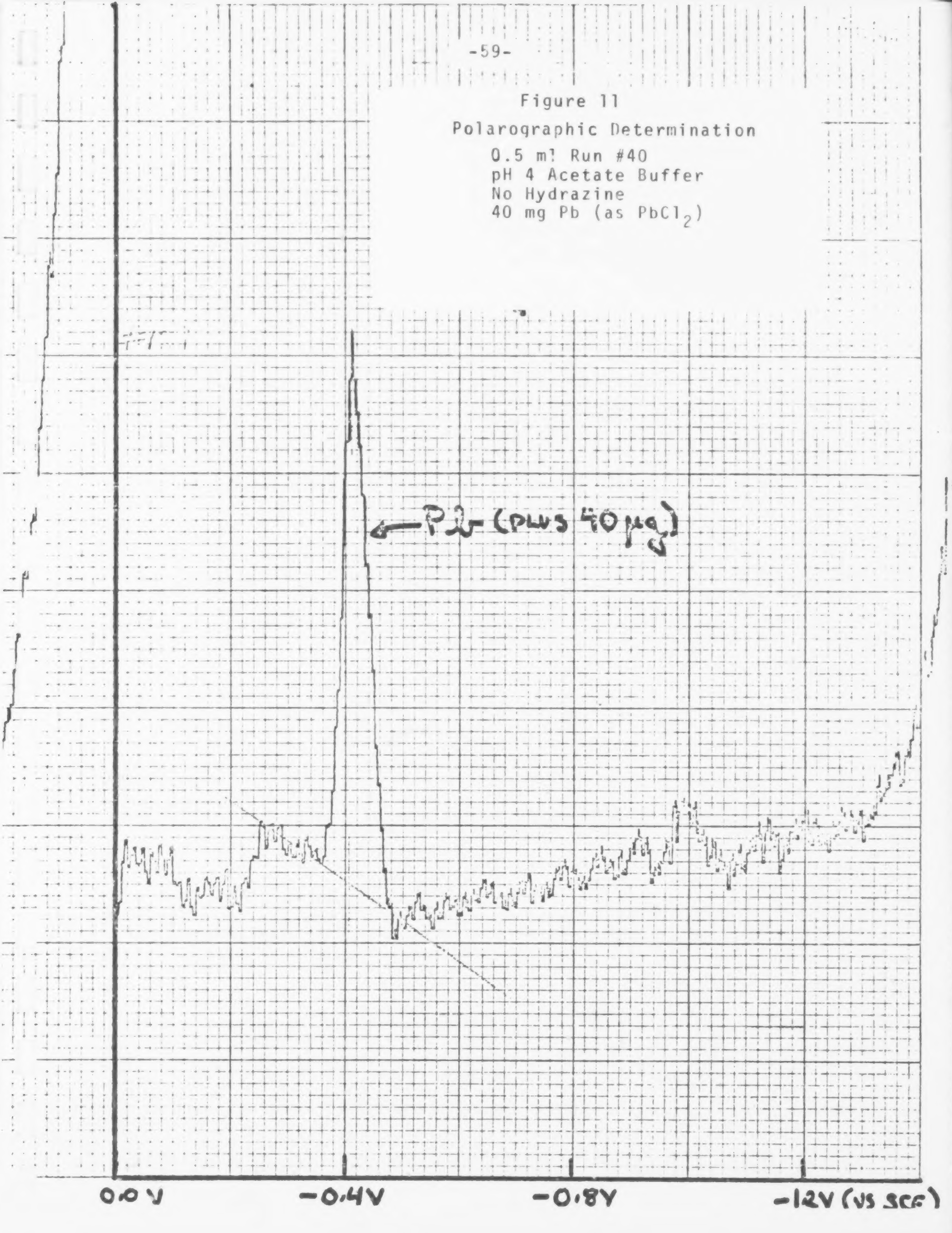


Figure 11

Polarographic Determination

0.5 ml Run #40
pH 4 Acetate Buffer
No Hydrazine
40 mg Pb (as $PbCl_2$)

Procedure

Pipet 2 ml of methanol sample into a 25-ml volumetric flask. Add 10 ml of pH 4 acetate buffer and dilute to volume with water. Transfer this solution to a polarographic cell and deaerate with oxygen-free nitrogen for ten minutes. Record a derivative pulse polarogram from 0 to -1.6 V vs. SCE. Add 2 ml of hydrazine reagent to the polarographic cell and deaerate for 5 minutes. Again, record the polarogram from 0 to 1.6 V vs. SCE.

Lead and aromatic ketones are determined from the waves obtained without hydrazine at the peak potentials listed above. Formaldehyde, higher aliphatic aldehydes, aromatic aldehydes, and aliphatic ketones can be determined from the second polarogram with hydrazine present.

All responses should be calibrated by addition of known amounts of standard compounds to actual runs. Peak heights are linear with concentration.

In this system, zinc has a peak potential of -1.00 V vs. SCE, but it can be differentiated from benzophenone by the fact that it possesses only one polarographic wave.

11. Organic Separation

Micro methods have been developed for the determination of the following in automotive exhaust particulate samples.

a) Benzene solubles and ultraviolet absorptivity
b) Phenolics
c) Total acidity
d) Ultraviolet fluorescence

a. Determination of Benzene Solubles and Ultraviolet Absorptivity

1) Scope

Samples obtained as scrapings from Andersen impingement plates or on sheets of fiberglass filters were used to quantitatively collect auto exhaust particulates. The following method can apply to particulate matter from industrial or urban air and exhausts whenever the filter can be physically extracted and does not produce an appreciable blank of benzene solubles.

The weight percent and relative ultraviolet absorbance of the benzene solubles were obtained, both based on total particulate collected. The weight percents were related to the total organic content, and the absorbance values related to the aromatic moieties present.

2) Principle

The samples are extracted with benzene and the residue weighed after evaporation of the filtered extract. The residue is dissolved in methanol and the absorbance quantitatively measured.

3) Interferences

Trace solvent impurities and equipment trace contamination could be the main sources of interferences. Detection and correction is accomplished by processing blanks and controls along with the samples. Organics present as metal salts are not accounted if insoluble in benzene. Any lead compounds soluble in benzene would give high results because the lead cation has appreciable absorbance in the ultraviolet region. Highly conjugated aliphatic compounds are not expected, but their presence would lead to higher absorbance values.

4) Apparatus

a) Spectrophotometer, Cary Model 14 or equivalent, and matched 1-cm cells.

b) Vacuum oven set at 45-55°C and storage desiccator to maintain vials at constant weight.

c) Balance, sensitivity ±0.02 mg.

d) Mechanical shaker.

e) Small mouth bottles and vials (2 x 7 cm) with Teflon-lined screw lids. The glass lips are ground flat with emery cloth to assure leak-proof seals.

f) Sintered glass, filter funnels (medium), volumetric flasks and pipets.

g) Steam heated bath and a nitrogen supply terminated with medicine dropper nozzles for evaporation under a stream of flowing nitrogen gas.

5) Reagents

a) Benzene, spectrophotometric grade. The UV-cutoff (absorbance of 1) should be less than 280 nm in a 1-cm cell; evaporation of 100 ml should produce less than 0.1 mg residue.

b) Methanol, spectroscopic grade. The UV-cutoff should be less than 210 nm in a 1-cm cell, and the evaporation of 100 ml should produce less than 0.1 mg residue.

6) Procedure

a) Weigh by difference to ±0.1 mg the collected particulates. Remove the particulates by scraping with a razor blade when Andersen plates are used, weigh to ±0.1 mg, transfer to an extraction bottle and extract using 10 to 50 ml of benzene for amounts 0.2 to 25 mg. When a sample on a glass-fiber filter is analyzed, cut the filter into small sections and transfer to an extraction bottle; extract using 50 to 600 ml of benzene for 0.01 to 0.7 g of collected particulate. Shake for a minimum of 4 hours. Tape the lids to prevent unscrewing and leakage.

b) Collect the extracts by filtration using sintered glass funnels. Transfer all filter segments to the funnel. Rinse several times with benzene, using a glass tamper to press dry the filter cake.

c) Evaporate most of the benzene in the filter flask by heating on the steam cone with a stream of nitrogen directed to the surface. Quantitatively transfer to vial, predried to constant weight of ±0.04 mg using benzene rinses. Complete the evaporation of the benzene as described. Do not let the benzene temperature exceed 60°C, and do not let the vial remain on the steam cone when evaporation is complete (Note 9b). Remove the last benzene trace by storing 5 minutes in a vacuum oven at 10 mm pressure and 45-55°C. Store in a desiccator containing barium oxide for at least 10 minutes to equilibrate, and weigh by difference the residue to ±0.04 mg.

d) Dissolve in approximately 1 ml/mg of methanol or a minimum of 5.00 ml. This dilution was used for various determinations (Note 9d).

e) Scan the base line characteristics of the spectrophotometer and cells from 460 to 220 nm with methanol in the sample and reference 1-cm cells. Then scan the appropriate, quantitative dilution of a small aliquot of (d) to have a net absorbance between 0.2 to 1.2 at 255 nm without changing the balance (Note 9c). Methanol is used in the reference cell. Record the net absorbance at 255 nm, the dilution, and the wavelength of prominent spectral features.

f) Repeat steps (a) through (e) using an unused porous glass filter as blank.

7) Calculations

a) Relative UV absorbance/mg particulate sample

$$\text{Rel UV/mg} = \frac{AVT}{B} \times \frac{1000}{mg_S}$$

where

A = net absorbance of benzene solubles at 255 nm of the dilution analyzed after correction for base line and blank

mg_S = particulate analyzed, mg

V = absorbance dilution volume, ml

T = volume containing all benzene solubles, ml

B = aliquot of T used in absorbance dilution, ml

b) Absorptivity (a)

$$a = \frac{AVT}{B\ (mg_R - mg_B)}$$

where

mg_R and mg_B are mg of benzene solubles from sample and blank respectively.

c) Relative UV absorbance of total particulate ($\times 10^{-3}$)

$$\text{Rel UV particulate} = \frac{AVT}{B} \times \frac{mg_P}{mg_S}$$

where

mg_P = mg total particulate on filter

d) Percent benzene soluble ($\%_B$)

$$\%_B = \frac{(mg_R - mg_B)}{mg_S} \times 100$$

8) Precision and Accuracy

Precision and accuracy cannot be calculated because known or duplicate samples were not analyzed. Results are most meaningful when 3 mg or more of benzene solubles is collected.

9) Notes

a) All equipment and containers must be cleaned using dichromate sulfuric acid, rinsed thoroughly and dried at 110°C to minimize trace contamination.

b) Valori (Reference 10) has shown that the loss of polynuclear aromatics during evaporation is low.

c) From 0.3 to 0.07 mg benzene solubles per ml of methanol is usually required to produce a net absorbance in the range indicated.

d) If insoluble material is present, transfer the contents to a preweighed centrifuge tube and centrifuge. Remove the clear liquor with a medicine dropper and return to the initial vial. Rinse the insolubles and inner surface of the tube with methanol several times. Remove the residual solvent and determine the weight of this residue as described in 6(c).

b. Determination of Phenolic Content

The weight percent phenolics in the benzene soluble fraction of the particulate have been obtained.

1) Principle

Phenolic materials produce a 20-30 nm shifting of an absorption peak when converted to the anionic form. The difference in absorption is measured at 295-300 nm of two solutions of equal concentrations, one containing excess KOH and the other excess HCl. This difference was used to calculate the amount of phenolics based on the calibrated response of p-phenylphenol.

The method was adapted to the characteristics of actual samples which showed a differential response at 295-300 nm, similar to p-phenylphenol, which shows a difference maximum at 297 nm and absorptivity of 120 nm. Different phenols show significant variations in location of the maximum and magnitude of absorptivity at 295-300 nm; thus the calculated values should be compared only to similar samples, and not taken as absolute values. Absolute values would necessitate isolation of the phenolic fraction with determination of absorptivity.

Analyses have shown significant differential absorbances at 410 and 450 nm, indicating the presence of unaccounted, colored (phenolic) materials.

2) Apparatus

a) Spectrophotometer, Cary Model 14 or equivalent, and matched 1-cm cells.

b) Vacuum oven set at 45-55°C and storage desiccator to maintain vials at constant weight.

c) Balance, sensitivity ±0.02 mg.

d) Mechanical shaker.

e) Small mouth bottles and vials (2 x 7 cm) with Teflon-lined screw lids. The glass lips are ground flat with emery cloth to assure leak-proof seals.

f) Sintered glass, filter funnels (medium), volumetric flasks and pipets.

g) Steam heated bath and a nitrogen supply terminated with medicine dropper nozzles for evaporation under a stream of flowing nitrogen gas.

3) Reagents

Alcoholic KOH, 1N. Dissolve 56.1 g KOH (assay 99.5% minimum) in 56 ml of distilled water, cool, and dilute with methanol to 1 liter at room temperature. Store in polyethylene bottle.

4) Procedure

a) Weigh by difference to ±0.1 mg the collected particulates. Remove the particulates by scraping with a razor blade when Andersen filters are used, weigh to ±0.1 mg, transfer to an extraction bottle and extract using 10 to 50 ml of benzene for amounts 0.2 to 25 mg. When a sample on a porous glass filter is analyzed, cut the filter into small sections and transfer to an extraction bottle; extract using 50 to 600 ml of benzene for 0.01 to 0.7 g of collected particulate. Shake for a minimum of 4 hours. Tape the lids to prevent unscrewing and leakage.

b) Collect the extracts by filtration using sintered glass funnels. Transfer all filter segments to the funnel. Rinse several times with benzene, using a glass rod to press dry the filter cake.

c) Evaporate most of the benzene in the filter flask by heating on the steam cone with a stream of nitrogen directed to the surface. Quantitatively transfer to vial, predried to constant weight of ±0.04 mg using benzene rinses. Complete the evaporation of the benzene as described. Do not let the benzene temperature exceed 60°C, and do not let the vial remain on the steam cone when evaporation is complete. Remove the last benzene trace by storing 5 minutes in a vacuum oven at 10 mm pressure and 45-55°C. Store in a desiccator containing barium oxide for at least 10 minutes to equilibrate, and weigh by difference the residue to ±0.04 mg.

d) Dissolve in approximately 1 ml/mg of methanol or a minimum of 5.00 ml.

e) Repeat steps (a) through (c) using an unused glass filter as blank.

f) Scan the base line characteristics of the matched, 1-cm cells from 680 to 220 nm with alcoholic KOH in the sample cell and with methanol containing 1 drop of concentrated HCl per 5 ml in the reference cell.

g) Without altering the balance, scan from 680 to 220 nm appropriate, equal aliquots of solution (d) each diluted to 5.00 ml to give a differential absorbance less than 0.5 at 300 nm with the material in the sample cell diluted using alcoholic KOH and that in the reference cell diluted using methanol containing HCl (1 drop/5 ml). Record the differential, net absorbance (ΔA_{300}) at 295-300 nm, the dilution and aliquot volumes, and the wavelength and differential absorbances of any peak responses greater than 300 nm.

h) Repeat (g) using solution from (e).

5) Calculations

a) Differential phenolic absorbance (ΔA)

The differential phenolic absorbance is calculated as obtained in 1-cm cells if 9 percent of the benzene soluble fraction were diluted to 5 ml using 1N KOH in methanol with a corresponding dilution using HCl in the reference cell.

$$\Delta A = \frac{\Delta A_{300} \times 0.018 \times V \times T}{B}$$

where

ΔA_{300} = measured difference, absorbance units
V = the dilution volume, ml
T = the volume containing all benzene solubles, ml
B = the aliquot of T used, ml
0.018 = obtained from $0.09 \div 5$

b) Micrograms (μg) of phenolics calculated as para-phenylphenol

$$\mu g = \Delta A \times 463 \text{ (Note 7a)}$$

c) Wt. percent phenolics in benzene solubles ($\%_{PB}$)

The weight percent phenolics is taken as the average of maximum and minimal values, based on exclusion and inclusion of the blank correction.

$$\%_{PB} = \frac{\mu g_P - 1/2\ \mu g_{PC}}{mg_R \times 10} \pm \frac{1/2\ \mu g_{PC}}{mg_R \times 10}$$

where

μg_P = the amount found in the sample, μg
μg_{PC} = the amount found in the blank, μg
mg_R = the benzene solubles from the sample, mg

d) Wt. percent phenolics in particulate sample ($\%_{PP}$)

$$\%_{PP} = \frac{\%_{PB} \times \%_B}{100}$$

where

$\%_B$ is calculated

$$\%_B = \frac{(mg_R - mg_B)}{mg_S} \times 100$$

6) Precision

Particulate samples of known composition were not analyzed. Known dilutions of p-phenylphenol showed a linear absorbance (295 nm) up to 0.6 within ±0.02. Blanks indicated a variability or contamination of 30 μg per run calculated as p-phenylphenol. The precision is dependent on sample size and phenolic content. The weight percent phenolics in benzene solubles is calculated as the difference of two calculations of maximum and minimum amounts. Precision (i.e. ±1/2 μg_{PC}) ranges from ±0.1 percent absolute with 19.8 mg of benzene solubles to ±0.3 percent for 4.7 mg and 1.1 percent for 1.2 mg.

7) Notes

The equation is derived from absorptivity (a).

$$a = \frac{\Delta A \times \text{volume}}{mg}$$

The absorptivity of p-phenylphenol is 120. Thus

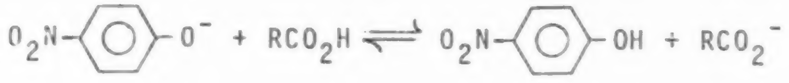
$$\mu g = \frac{\Delta A \times 5 \times 10^3}{120} \times \frac{100}{9}$$

The factor 100/9 relates the value of the 9 percent aliquot to that of all of the benzene soluble fraction.

c. Determination of Acidity

1) Principle

Sodium 4-nitrophenate is used as both indicator and excess titrant to measure acidity.



The change in the absorbance of the 4-nitrophenate anion is determined spectroscopically in the presence and absence of the sample. The difference is related to the acidity calibrated using known benzene acid mixtures.

2) Interferences

Since the acidity is related to benzoic acid, the results are most meaningful in relative comparisons. The acidic materials in the benzene soluble fraction have been characterized via infrared as organic carboxylic acids. Weaker acids are partially accounted for, and strong acids would be excessively accounted. Benzoic acid is 30.4 percent ionized and phenol only 4.7 percent. Phenol produces one-sixth the indicator absorbance change as the same weight of benzoic acid.

Inert, colored impurities do not interfere because the absorbance of the sample is used to establish a base line. Unsuspected interferences can be detected by variations in certain spectral features. Acidity is determined by a decrease of the absorbance peak at 390 nm which is related to the 4-nitrophenoxide anion. Acidity can also be determined by an increase of the absorbance peak at 310 nm, related to the unionized 4-nitrophenol. The ratios of $\Delta A_{310}/\Delta A_{390}$ were -0.53 ±0.04 when pure benzoic acid and phenol were used. Gross interferences are detected by observed ratio variations greater than -0.5 ±0.2. The exact variation from -0.53 can be utilized to calculate an estimated deviation. The indicator system also shows an isosbestic at 335-340 nm; the difference in absorbance should thus agree closely with that of the sample less indicator if intereferences are absent. The magnitude of the disagreement can be used as a measure of interference.

It was found that some samples contained a yellow, unknown impurity with an absorbance peak at 380 nm, shifting to 400-450 nm upon addition of excess caustic. This shift is observed when determining the phenolic content described earlier. Maximum interferences calculated from spectral data indicates that the acidity results could be low by 10 to 30 percent. Maximum interference is not expected because calculated corrections in most cases produced abnormal ratios of $\Delta A_{310}/\Delta A_{390}$. Minimal interference is calculated to be less than 2 percent relative, assuming that the unknown impurity is phenolic and only 5 percent ionized.

3) Apparatus
   a) Spectrophotometer, Cary Model 14 or equivalent, and matched 1-cm cells.
   b) Vacuum oven set at 45-55°C and storage dessicator to maintain vials at constant weight.

The absorptivity of *p*-phenylphenol is 120. Thus

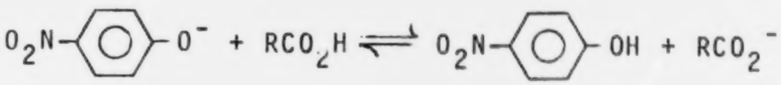
$$\mu g = \frac{\Delta A \times 5 \times 10^3}{120} \times \frac{100}{9}$$

The factor 100/9 relates the value of the 9 percent aliquot to that of all of the benzene soluble fraction.

c. Determination of Acidity

1) Principle

Sodium 4-nitrophenate is used as both indicator and excess titrant to measure acidity.



The change in the absorbance of the 4-nitrophenate anion is determined spectroscopically in the presence and absence of the sample. The difference is related to the acidity calibrated using known benzene acid mixtures.

2) Interferences

Since the acidity is related to benzoic acid, the results are most meaningful in relative comparisons. The acidic materials in the benzene soluble fraction have been characterized *via* infrared as organic carboxylic acids. Weaker acids are partially accounted for, and strong acids would be excessively accounted. Benzoic acid is 30.4 percent ionized and phenol only 4.7 percent. Phenol produces one-sixth the indicator absorbance change as the same weight of benzoic acid.

Inert, colored impurities do not interfere because the absorbance of the sample is used to establish a base line. Unsuspected interferences can be detected by variations

c) Balance, sensitivity ±0.02 mg.

d) Mechanical shaker.

e) Small mouth bottles and vials (2 x 7 cm) with Teflon-lined screw lids. The glass lips are ground flat with emery cloth to assure leak-proof seals.

f) Sintered glass, filter funnels (medium), volumetric flasks and pipets.

g) Steam heated bath and a nitrogen supply terminated with medicine dropper nozzles for evaporation under a stream of flowing nitrogen gas.

4) Reagents

a) 4-Nitrophenate Indicator Solution. Sodium 4-nitrophenate is prepared by first dissolving 5.16 g 4-nitrophenol (Eastman Kodak) in 44.6 ml 0.75N sodium hydroxide in ethanol. The solution is evaporated to dryness. The residue is triturated and washed using 200 ml petroluem ether, and then dried at 1 mm at 50°C for 2 hours.

Then 11 to 12 ±0.1 mg is dissolved and diluted to 100.0 ml using spectroscopic-grade methanol.

b) Benzoic acid, primary standard grade.

5) Calibration

a) Weigh 19 to 21 ±0.05 mg of benzoic acid into a 500-ml volumetric flask, dissolve and dilute to volume using methanol.

b) Add 1.00, 2.00, and 5.00-ml aliquots of solution from (e) page 68, respectively to 25-ml volumetric flasks. Then add a 2.50-ml aliquot of the 4-nitrophenate indicator solution to each flask and also to a fourth flask to be used as a blank. Dilute all to volume using methanol and mix the contents.

c) Adjust the spectrophotometer to permit recording a negative absorbance of 0.25 at 390 nm. Determine the base line characteristics from 280 to 400 nm, using the blank solution in the sample and reference 1-cm, matched cells. Then measure the difference absorbances of the three dilutions vs. the blank from 280 to 400 nm as illustrated in Figure 12.

d) The absorbances at 390 and 310 nm are plotted vs. micrograms of benzoic acid per 25 ml as illustrated in Figure 14.

6) Procedure

a) Add appropriate and equal aliquots of solution (d) page 68, to two of three 5.00-ml volumetric flasks. Add 0.50 ±0.2 ml of the indicator solution to the first and third flasks. Dilute all three flasks to volume using methanol and mix the contents.

b) Measure the absorbance of the sample in the second flask from 480 to 240 nm in a 1-cm cell with methanol in the reference cell. A typical scan is shown as I in Figure 13.

c) Measure the absorbance difference of the other two solutions from 480 to 240 nm without changing the balance. The solution containing both sample and indicator is placed in the sample cell. A typical scan is shown as II in Figure 13.

7) Calculations

a) Acidity as micrograms of benzoic acid in benzene solubles ($\mu g_{\phi CO_2H}$).

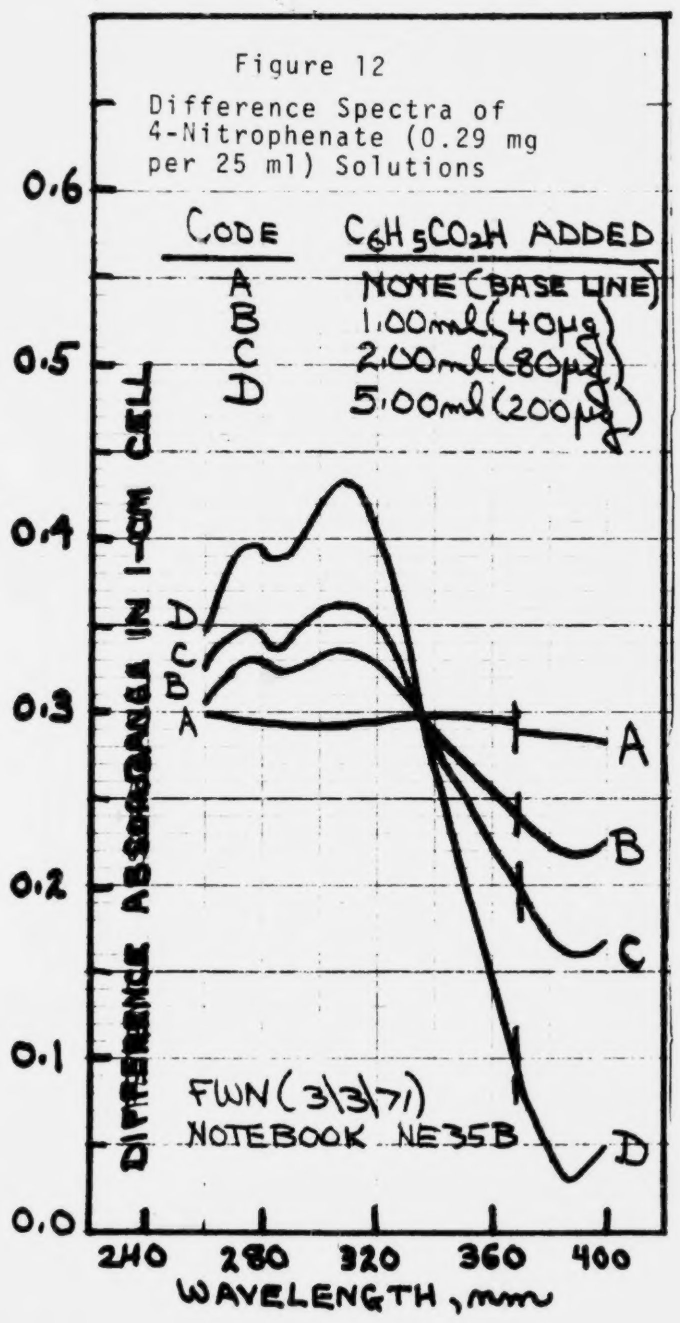


Figure 12

Difference Spectra of 4-Nitrophenate (0.29 mg per 25 ml) Solutions

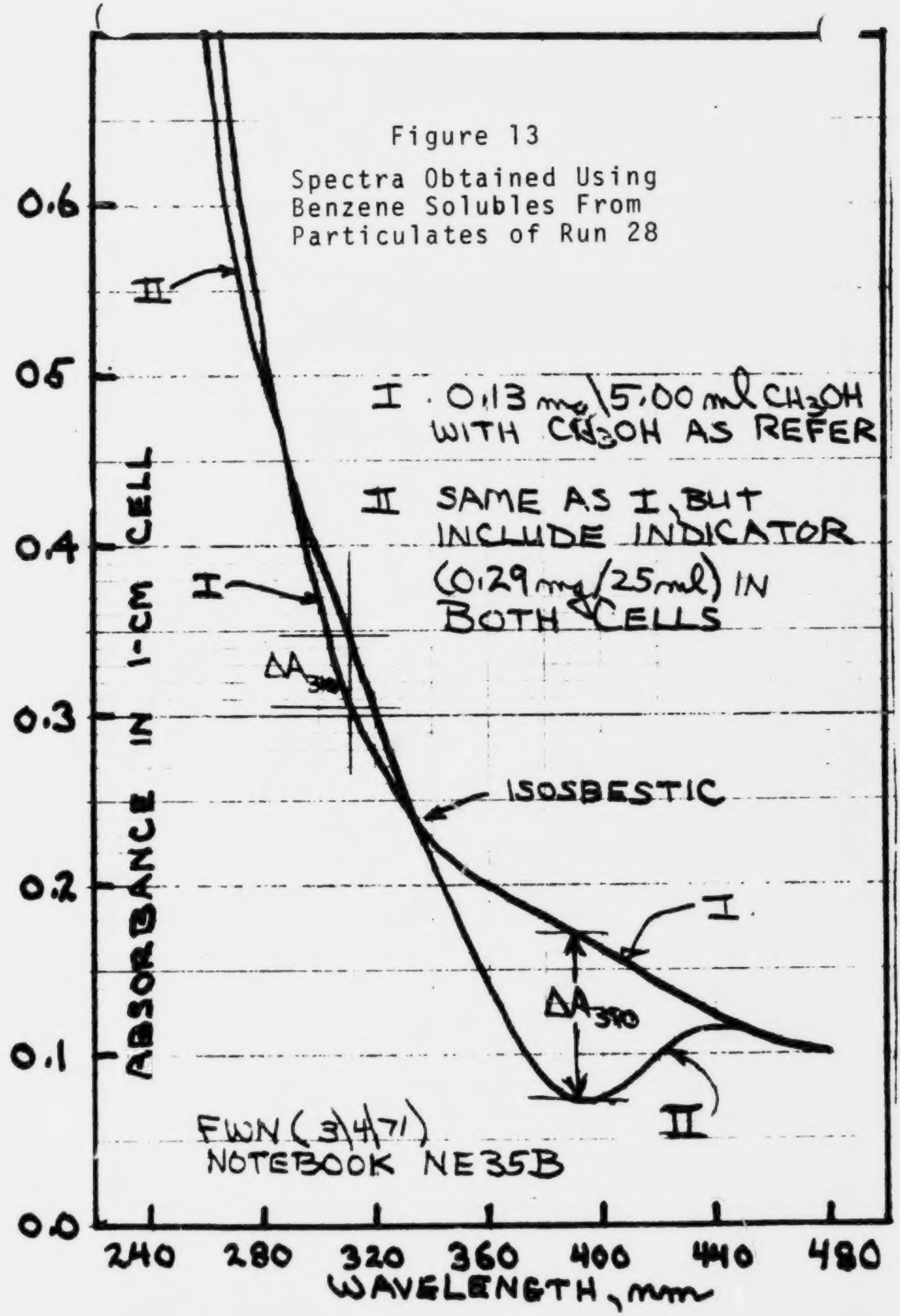
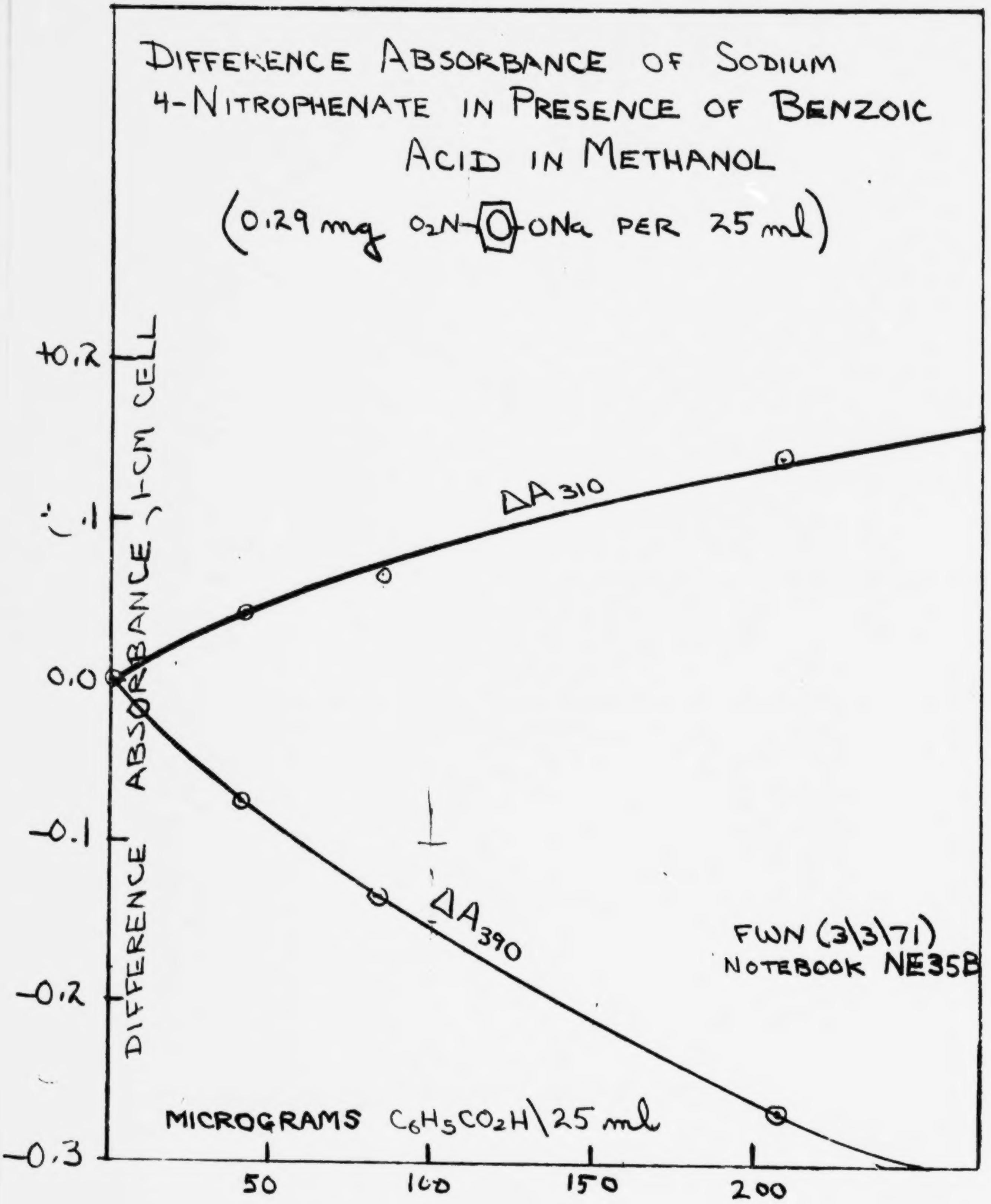


Figure 13

Spectra Obtained Using Benzene Solubles From Particulates of Run 28

Figure 14



DIFFERENCE ABSORBANCE OF SODIUM 4-NITROPHENATE IN PRESENCE OF BENZOIC ACID IN METHANOL

(0.29 mg O_2N-⌬-ONa PER 25 ml)

$$\mu g_{\phi CO_2H} = \frac{W \times V \times T}{25 \times B}$$

where

W = the value obtained from the calibration graph based on the measured value of ΔA_{390}, μg/25 ml

V = the absorbance dilution volume, ml

T = the volume containing all benzene solubles, ml

B = the aliquot of T used, ml

b) Acidity of particulates calculated as percent benzoic acid (% A_P)

$$\% \ A_P = \frac{(\mu g_{\phi CO_2H} - \mu g_{BC})}{mg_S \times 10}$$

where

μg_{BC} = the amount calculated for the blank, μg

c) Acidity of benzene solubles calculated as percent benzoic acid (% A_R)

$$\% \ A_R = \frac{(\mu g_{\phi CO_2H} - \mu g_{BC})}{mg_R - mg_B)10}$$

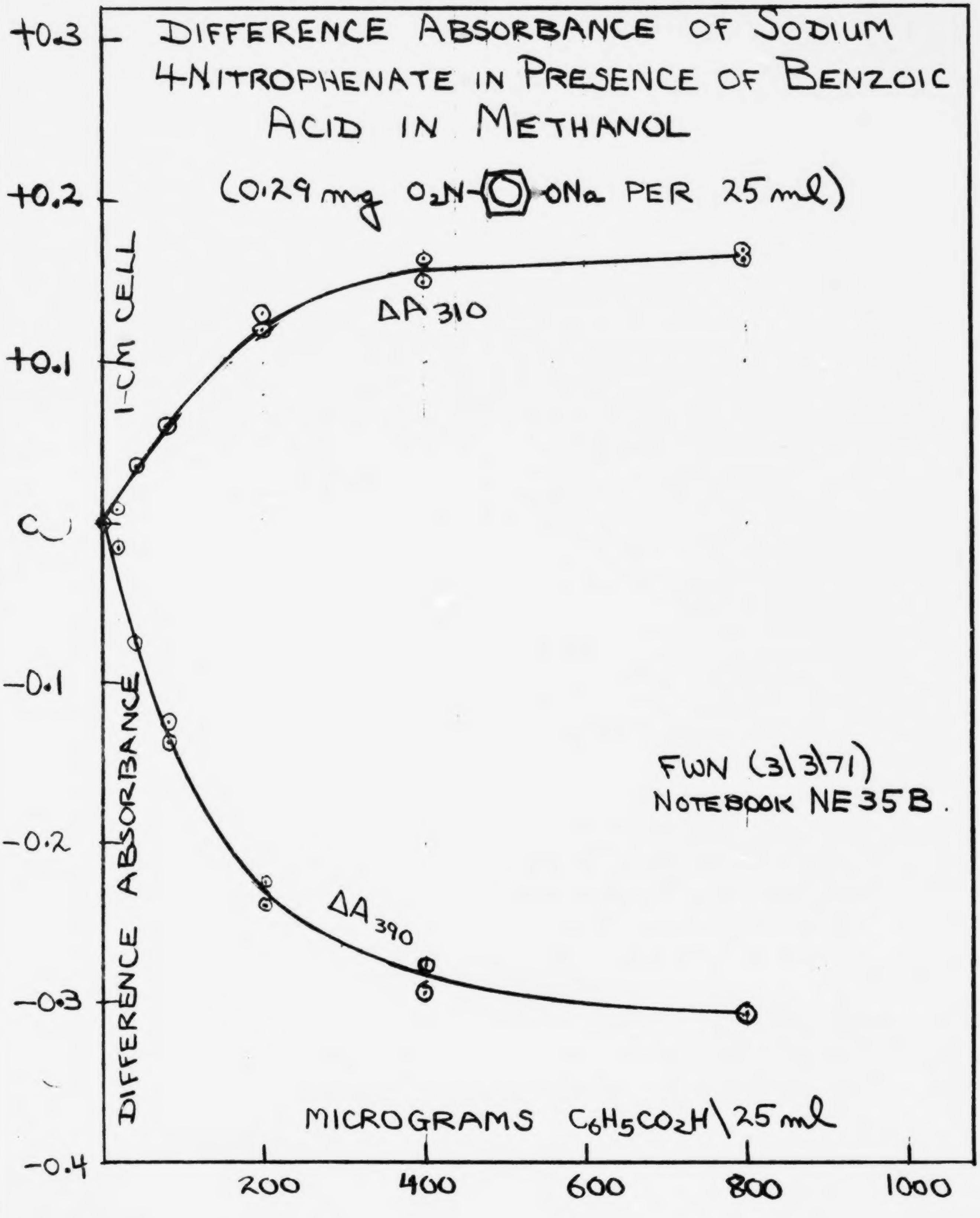
8) Precision

Particulate samples of known composition were not analyzed. Precision and accuracy are dependent on the relative amounts in the samples and blanks. Unused filters and solvent showed acidity blanks of ±15 μg calculated as benzoic acid.

9) Notes

a) The extreme non-linearity at higher concentrations is shown in Figure 15.

Figure 15


DIFFERENCE ABSORBANCE OF SODIUM 4NITROPHENATE IN PRESENCE OF BENZOIC ACID IN METHANOL
(0.29 mg O₂N-⌬-ONa PER 25 ml)
+0.3
+0.2
+0.1
0
-0.1
-0.2
-0.3
-0.4
DIFFERENCE ABSORBANCE 1-CM CELL
ΔA 310
ΔA 390
FWN (3\3\71)
NOTEBOOK NE35B.
MICROGRAMS C6H5CO2H\25 ml
200
400
600
800
1000

b) An appropriate aliquot is one producing an absorbance difference at 390 nm less than -0.25 as shown in Figure 13. The response sensitivity decreases with larger amounts as shown in Figure 15. An appropriate aliquot in one series was 0.20 ml of solution containing from 0.5 to 7 mg/5 ml of the benzene soluble fraction.

d. Ultraviolet Fluorescence

Automobile exhaust particles were extracted with cyclohexane and the ultraviolet and fluorescence spectra were run. The absorbance at 255mμ and the fluorescence area using an exciting wavelength of 290mμ were used to calculate relative amounts of UV absorbing and fluorescent compounds present. The total amount of absorbing and fluorescent compounds do not seem to vary significantly from one run to the next; however, the amount present in a given sample weight increases with non-leaded gasoline and with the decreasing particle size.

A quick standard procedure for the determination of relative amounts of aromatic organic materials present in automobile exhaust particles was developed. Since limited funding was available to develop separation procedures and determine individual components, a general procedure of determining the ultraviolet absorbance and a value for fluorescence was used. These techniques detect the aromatic organics present including the poly-nuclear aromatics. Samples were received on Andersen glass plates and in bottles. The bottled samples had been obtained by sweeping out the inside of the dilution tube and from trays that were located beneath slits in the dilution tube.

1) Procedure

a) Sample Handling - The particulate matter from the Andersen glass plates was scraped loose with a razor blade and transferred to a small tared watch glass with a small camel hair brush. The sample weight was obtained using a Mettler micro balance. The sample was then transferred to a 15 ml screw cap centrifuge tube (the cap of the tube should be lined with foil or Teflon) and 2-10 ml of cyclohexane (purified by passing through a silica column) was added depending on expected organic concentration.

Andersen plates with <1 mg of particulate present were handled by placing the glass plate in a petri dish and adding 5 ml of the cyclohexane. The dish was rotated in such a manner as to rinse the filter thoroughly; then the solution was transferred to a screw-cap centrifuge tube. The procedure was repeated with an additional 5 ml of solvent and thy solution evaporated to 2 ml by passing a stream of nitrogen over the solution. The sample weight was obtained by weighing the filter before and after use.

Approximately 10 mg of the bottled samples were weighed in a small porcelain boat and transferred to the 15 ml screw-cap centrifuge tubes and 10 ml of solvent added. The centrifuge tubes were capped tightly and the caps prevented from loosening by wrapping with rubber tape. The tubes were placed on their sides in an automatic shaker and shaken for a minimum of 5 hours. The rubber tape was removed and the solution centrifuged until clear and then the liquid was decanted into screw-cap bottles.

b) UV Absorption Measurements and Calculations - A Cary Model 15 spectrophotometer was used with 1-cm silica cells. When adequate solution was not available, a 1-cm semi-micro cell (volume ≈0.5 ml) was used. The solutions were scanned from 400-220mμ, diluting when necessary to keep the absorbance less than 2.0. All the samples gave very similar shaped spectra with a distinct maximum at 255mμ. The absorbance at 255mμ was used as a measure of the organic content. A relative value of UV absorbing material present was obtained by calculating the absorbance for 1.0 mg of residue in 1.0 ml of solvent x 1000. An estimation of the relative total absorbing material present on an Andersen plate can be obtained by multiplying the sample weight in mg times the number obtained above.

c) Fluorescence Measurements and Calculations - An Aminco-Bowman spectrophotofluorometer equipped with a Moseley model 135AMX-Y recorder and standard 1-cm cells, polished on all sides, was used for the fluorescence measurements. When adequate solution was not available, a semi-micro cell (Volume ≈0.5 ml), polished on all sides, was used by placing the narrow portion facing the excitation source and the wide portion (1 cm of solution) facing the detector. Various excitation wavelengths were examined (290, 330, and 353mμ) with 290mμ giving, in general, the most detailed and intense spectra. Exceptions to this are Plate 5 from Runs 9, 11, 12, 13, 14, and 16 and all of Run 17, where the 353mμ exciting wavelength gives a more intense spectra (353mμ is used by some authors for determining poly-nuclear aromatic compounds). The area in in.^{2} x 100 under the fluorescence peaks at an excitation wavelength of 290mμ was determined with a planimeter. A relative value of the fluorescence area for 1.0 mg of residue in 1.0 ml of solvent at a sensitivity setting of 0.01, with all slits at 2 mm, the wavelength (x) scale on the recorder set at 20 fixed and the intensity (y) scale on the recorder set at 5 fixed. An estimation of the relative total fluorescent material present on an Andersen plate can be obtained by multiplying the sample weight in mg times the number obtained above.

e. The Determination of Benzo(α)pyrene in Auto Exhausts

Samples of auto exhaust particulate collected on Andersen plates and on 142 mm glass fiber filters were submitted for the determination of benzo(α)pyrene. Weights of the particulate were provided by weighing the filters on a four-place balance before and after exposure to the diluted auto exhaust. Particulate weights varied from 0.2-35.2 mg.

Procedure:

When available a sample of at least 10 mg (on either one or two filter papers) was used for analysis. The filters were folded and rolled with the particulates toward the inside of the roll and tied with copper wire. The rolls were Soxhlet extracted for at least six hours (with siphoning four to six times per hour) with 75 ml of benzene. The extracts were evaporated under a stream of filtered air at room temperature to ∿3 ml. This concentrate was filtered through a M-fritted glass filter into a tared vial. The flask and filter were washed three times with ∿2 ml of benzene for each wash. The combined filtrates were evaporated to dryness at room temperature with a stream of filtered air.

The residues obtained from both sample and blank filters were weighed and the difference between them designated "benzene soluble weight" for each sample. The residue was dissolved in 0.2 ml of methylene chloride and a 10-40 μl aliquot was spotted in 2-μl increments of a pre-conditioned Alumina TLC plate along with a known standard of benzo(α)pyrene in methylene chloride. The TLC plates were conditioned by heating at 120°C for 1.5 hours and desiccating overnight in a 45 percent relative humidity chamber (saturated aqueous zinc nitrate). The TLC plate was developed in an unsaturated tank containing 20 ml of ethyl ether in 200 ml of n-pentane to a height of 15 cm

(~45 minutes). The benzo(α)pyrene spots were identified by comparison of R_f's with that of the standard spot under an ultraviolet lamp. The spots, marked with a pencil, were circumscribed with a #15 cork borer and scraped from the plate into vials. All TLC work was performed as much as possible in a dimly lighted area to avoid decomposition of the benzo(α)pyrene. Five ml of 5 percent acetone in n-pentane was added to the alumina in the vial and it was agitated for 15 minutes on a mechanical shaker. The slurry was filtered through a F sintered glass filter into a vial, washing the alumina four times with ~2 ml of 5 percent acetone in n-pentane with a 45-second soak period between each wash. The combined filtrates were evaporated to dryness at room temperature using a stream of filtered air. The benzo(α)pyrene residue was taken up in 2.0 ml of concentrated sulfuric acid. This solution was evacuated for five minutes to remove trapped air bubbles and its fluorescence was measured in a 1-cm cell at 540 nm while exciting at 470 nm on an Amino-Bowman Spectrophotofluorometer using a #4 slit arrangement and a sensitivity of 30.

Standards and blanks were carried through the entire TLC procedure. The blanks were subtracted from all fluorescence readings and the net fluorescence values for each sample were used to calculate the amount of benzo(α)pyrene present. Throughout all steps in the procedure, the sample were refrigerated when not actually being processed and exposure of the samples to light was kept at a minimum.

IV. EXPERIMENTAL RESULTS

A. INTRODUCTION

Results are presented in this section in much the same order as is evident in the Procedures Section. There are many complex relationships to be observed between fuel, oil, and particulate trace metals as an example, which will be explored in depth in the Discussion Section rather than here. Due to the complexity of designating each specific run in the ensuing tables and figures, each will be referred to by run number. A ready reference table (Table 10) is included for convenience in relating these run numbers to such details.

Results are presented in final compiled form. Appendices providing the basic data from which compilations have been based are provided where appropriate. Details regarding specific analytical procedures have been discussed in detail in the preceding (Experimental Procedures) section of this report.

B. ENGINES AND VEHICLES

The following engine and vehicle types have been used during this study. More than one of each type may have been used, for example, the Chevrolet 350 CID equipped vehicles. [Note Table 11 (Run Number Designations).]

TABLE 11
TEST ENGINES AND VEHICLES

Test Engines

1970 Chevrolet	350 CID	2 bbl	V-8
1971 Pontiac	400 CID	2 bbl	V-8
1971 Chrysler	383 CID	2 bbl	V-8

Test Vehicles

1969 Chevrolet Impala	350 CID
1970 Chevrolet Impala	350 CID
1971 Chevrolet Impala	350 CID
1970 Ford Galaxy 500	351 CID
1971 Plymouth Fury III	318 CID
1969 Dodge Charger	440 CID

Engine specifications for the dynamometer studies are listed below. These engines were set to manufacturer's specifications for each respective model year.

1970 Chevrolet 350 CID V-8

Spark plugs	AC 455 .035" gap
Points dwell	28-32°
Timing	4° BTC
Idle Speed	780 rpm
Carburetor	2 bbl Rochester
Horsepower	255 @ 4800 rpm
Compression ratio	9.0:1

1971 Pontiac 400 CID V-8

Spark plugs	AC R475 .035" gap
Points dwell	30° .016" gap
Timing	8° BTC
Idle speed	750 rpm
Carburetor	2 bbl
Horsepower	265 @ 4400 rpm
Compression ratio	8.2:1

1971 Chrysler 383 CID V-8	
Spark plugs	Champion J11Y .035" gap
Points dwell	30-34°
Timing	0°
Idle speed	750 rpm
Carburetor	2 bbl
Horsepower	275 @ 4400 rpm
Compression ratio	8.5:1

C. DILUTION TUBE

1. Dilution Ratios

Table 12 indicates the average air-exhaust dilution ratio at the sampling zone of the dilution tube for each specific run by run number. Note that engine dynamometer runs use only one-half the engine exhaust while vehicle runs use the full exhaust. Dilution ratios for cycled vehicle studies are based upon the average vehicle exhaust output volume for the cycle. The tube is designed to operate at 520 scfm (standard cubic feet per minute), rather than monitoring a constant dilution ratio between engine and vehicle tests.

2. Dilution Tube Profile - Sampling Zone

The majority of the mass emission rate and cumulative mass distribution data depends upon the assumption that a true proportional sample is taken at the sampling zone. In order to determine the stability of the sampling zone, several evaluations have been conducted as noted below:

- a. Engine/Vehicle at Cruise Condition
  - 1) Temperature profile
  - 2) Flow rate profile
  - 3) Mass profile
- b. Vehicle Under Cyclic Operation
  - 1) Temperature variations at single point in sampling zone
  - 2) Flow rate variations at single point in sampling zone

TABLE 12

DILUTION TUBE AIR-EXHAUST RATIOS AND FLOW RATES BY RUN NUMBER

ENGINE STAND RUNS			CHASSIS DYNAMOMETER RUNS (Steady State Operation)		
Run No.	Air/Exhaust Dilution Ratio	Sampling Zone Flow Rate (cfm)	Run No.	Air/Exhaust Dilution Ratio	Sampling Zone Flow Rate (cfm)
3	12.64	497.80	24	5.22	526.80
4	11.39	494.52	25	6.47	525.63
5	11.74	509.10	27	5.00	532.90
6	11.78	518.15	28	4.39	524.00
7	11.91	518.76	30	3.96	524.00
8	11.74	524.00	33	4.54	520.32
9	11.95	522.56	34	4.14	519.89
11	11.93	520.94	37	6.78	522.76
13	11.89	521.11	38	5.70	526.00
16	11.33	524.92	41	5.04	525.60
18	13.23	513.52	42	6.60	525.60
19	12.48	522.59	43	6.13	522.77
20	13.13	535.69	44	4.58	520.00
21	11.34	522.58	50	4.32	508.44
22	11.77	519.77	54	3.39	522.17
23	12.13	522.59	58	5.58	524.00
29	10.11	524.80	61	5.20	524.00
31	10.10	527.65	63	5.37	524.00
32	9.94	520.30	65	4.76	524.00
40	10.51	525.63	67	--	524.21
44	10.78	524.47			
52A	10.82	524.46			
52B	25.68	522.36			
52C	24.48	522.36			
52D	10.90	521.54			
56B	32.76	522.30			
56C	13.20	522.60			
59	12.06	520.31			

Table 13 shows the flow rates and temperature profiles in both planes numerically. Figure 16 indicates the temperature profile in the horizontal and vertical planes in the sampling zone under vehicle/engine cruising mode (a.1 above). Likewise Figure 17 indicates the flow rate profile similarly (a.2 above) using an Alnor Series 6000 Velometer.

Table 14 shows the dilution tube flow profile both horizontally and vertically during steady-state operation of a vehicle on the chassis dynamometer using a Model 60 Anemotherm velocity meter. This data is shown graphically in Figure 18. Table 15 shows dilution tube flow profile taken from an engine stand run using the same instrument as above. Again this data appears grahically in Figure 19.

It can be noted that the flow is relatively constant in the center portion of the tube and that there are variations near the walls of the tube. It was also noted that they were usually lower at the entry port than on the far wall. To investigate this, an experiment was run where the tube was probed from right to left horizontally and then from left to right. The values were recorded in both cases. In the right (entry for probe) to left, the right values were lower than center and the left values were higher. When the tube was probed from left to right, the left (probe entry) values were lower and the right were higher. When an average of readings was taken, the data resulted in nearly a straight line. Apparently air leakage around the probe entry port, tube wall temperature and probe design make the differences in flow readings at the walls.

The mass profile in the sampling zone has been determined by two methods: 1) Comparison of actual collected particle mass in the Andersen separators and/or 4 cfm filters where two or

TABLE 13

DILUTION TUBE SAMPLING ZONE TEMPERATURE
FLOW RATE PROFILE
ENGINE DYNAMOMETER

Vertical Probe			Horizontal Probe	
Air Flow (fpm)	Temp. °F	Distance From Wall	Air Flow (fpm)	Temp. °F
410	170	2"	385	168
410	170	3"	385	170
410	171	4"	390	171
405	171	5"	390	171
400	171	6"	405	171
400	171	7"	400	172
400	171	8"	395	172
400	171	9"	390	172
395	170	10"	400	172
400	170	11"	400	172
405	169	12"	405	171
380	167	13"	410	171
390	167	14"	420	169

Temperature Range	Vertical Profile:	167-171°F	2.2%
	Horizontal Profile:	168-172°F	2.2%
	TOTAL	167-172°F	2.9%
Flow Rate Range	Vertical Profile:	380-410 Units	7.9%
	Horizontal Profile:	385-420 Units	9.0%
	TOTAL	380-420	10 %

Figure 16

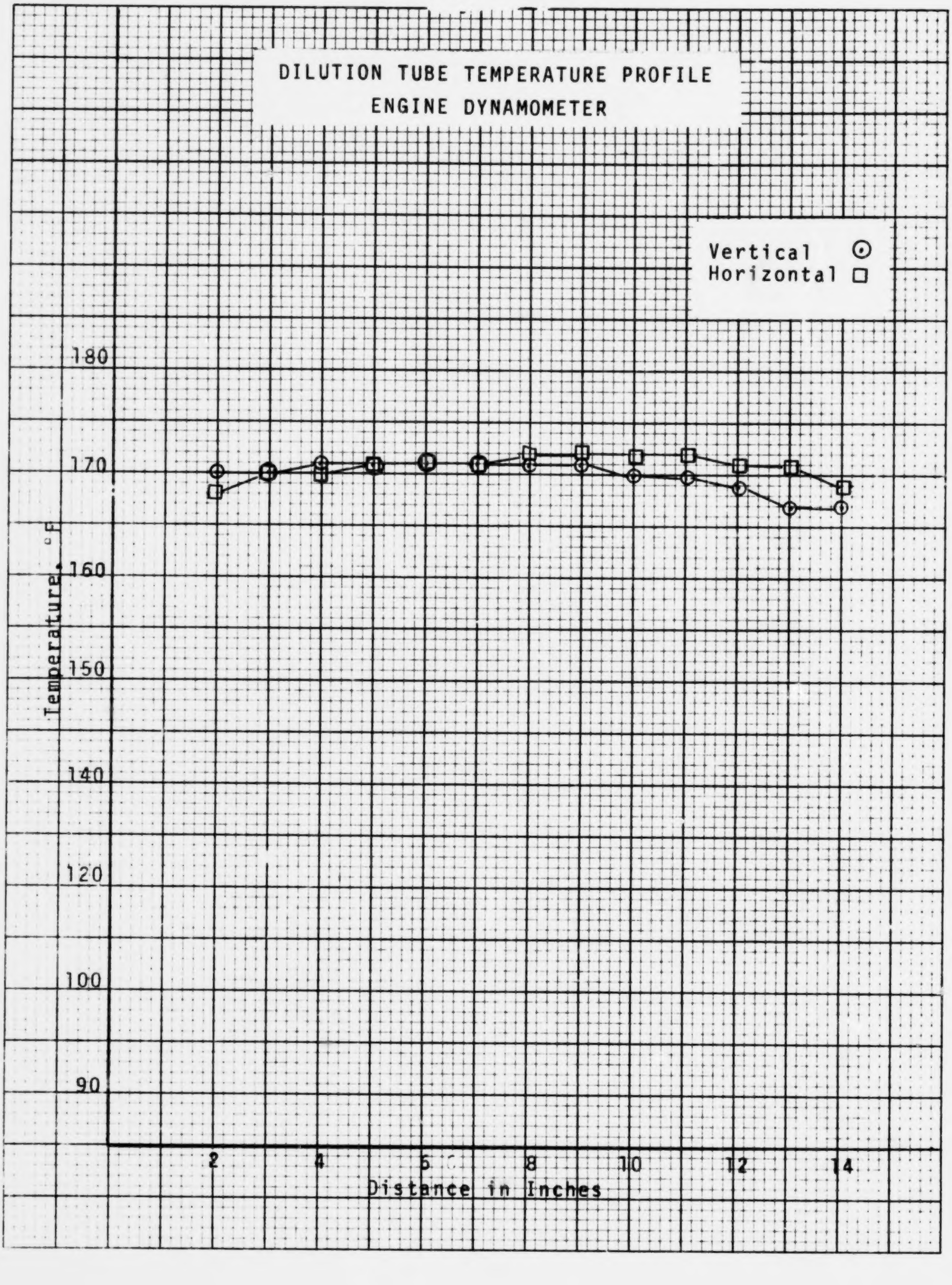

DILUTION TUBE TEMPERATURE PROFILE
ENGINE DYNAMOMETER
Vertical ⊙
Horizontal □
180
170
160
150
140
120
100
90
Temperature, °F
2
4
6
8
10
12
14
Distance in Inches

Figure 17

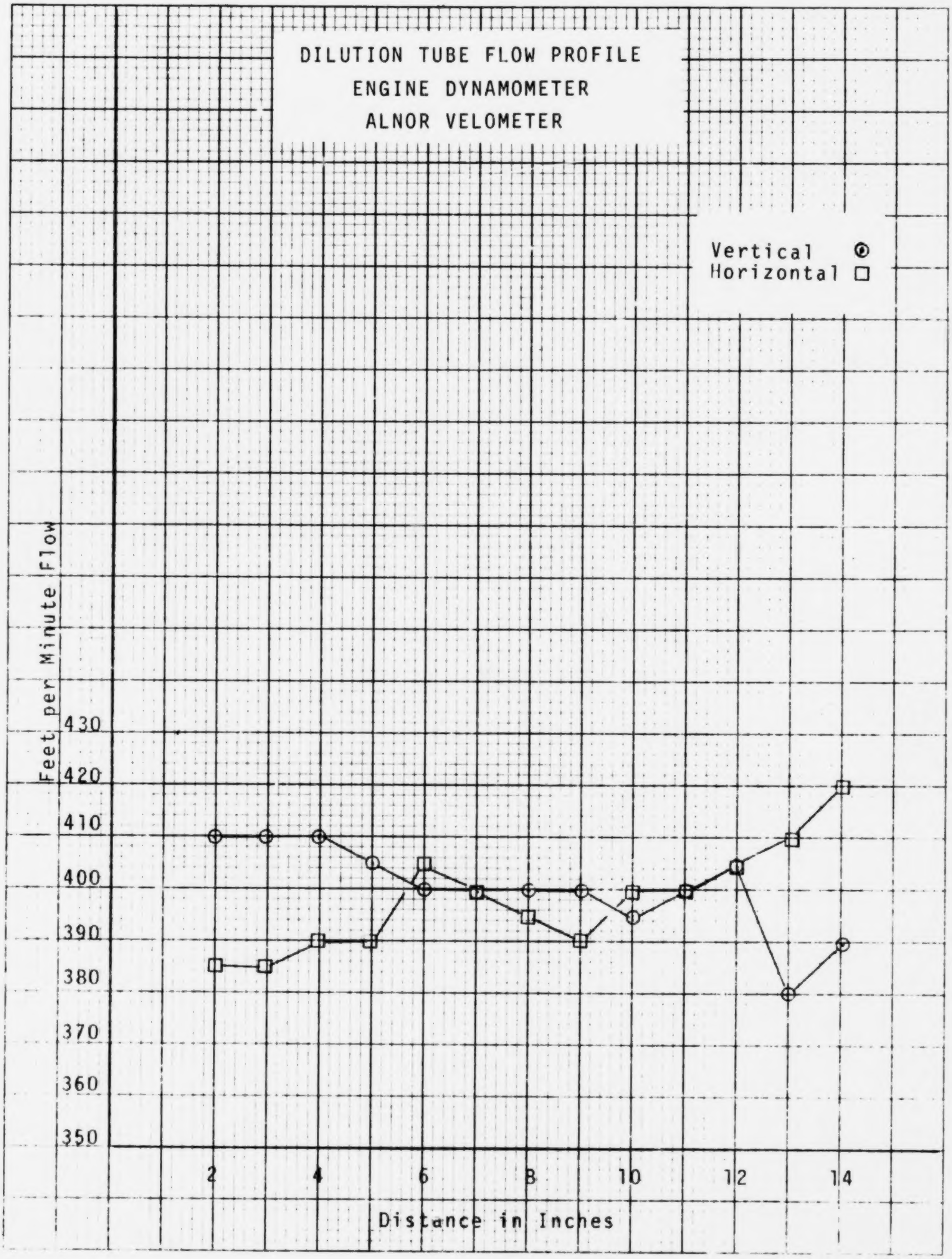

DILUTION TUBE FLOW PROFILE
ENGINE DYNAMOMETER
ALNOR VELOMETER
Vertical ⊙
Horizontal □
Feet per Minute Flow
430
420
410
400
390
380
370
360
350
2
4
6
8
10
12
14
Distance in Inches

Figure 18

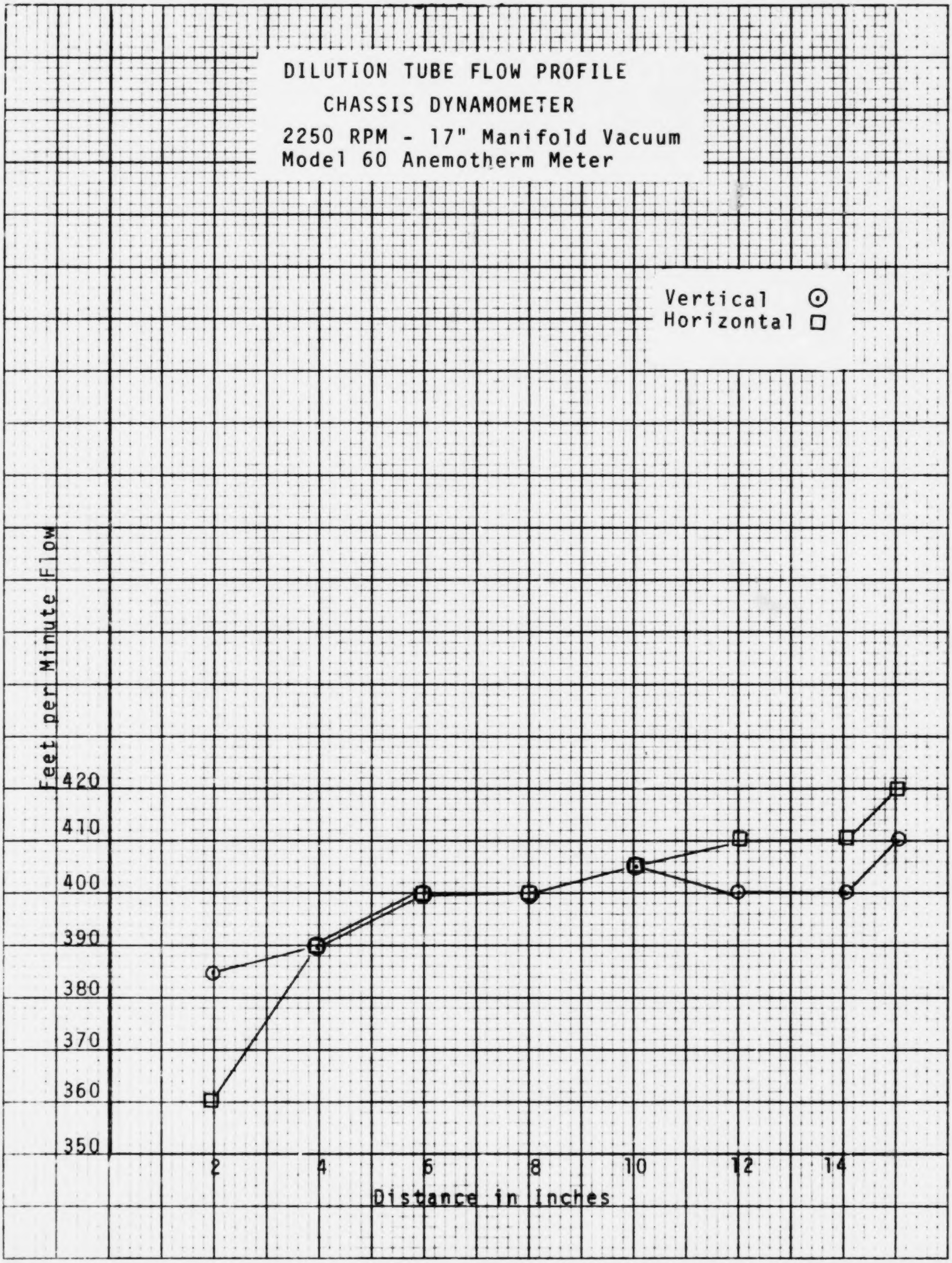

DILUTION TUBE FLOW PROFILE
CHASSIS DYNAMOMETER
2250 RPM - 17" Manifold Vacuum
Model 60 Anemotherm Meter
Vertical ⊙
Horizontal □
Feet per Minute Flow
420
410
400
390
380
370
360
350
2
4
6
8
10
12
14
Distance in Inches

Figure 19

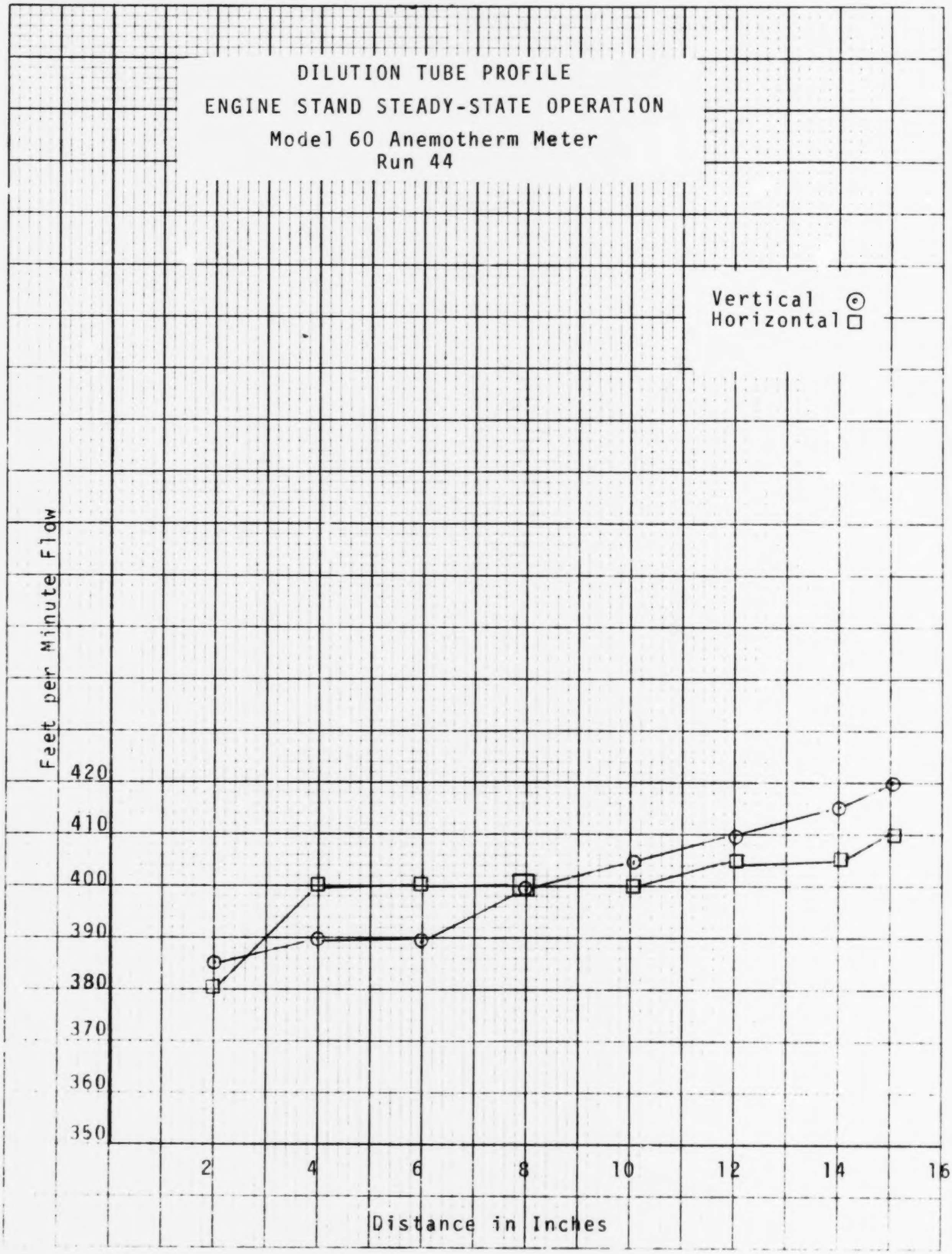

DILUTION TUBE PROFILE
ENGINE STAND STEADY-STATE OPERATION
Model 60 Anemotherm Meter
Run 44
Vertical ⊙
Horizontal ☐
Feet per Minute Flow
420
410
400
390
380
370
360
350
2
4
6
8
10
12
14
16
Distance in Inches

TABLE 14
DILUTION TUBE FLOW PROFILE
CHASSIS DYNAMOMETER
2250 RPM - 17" Manifold Vacuum

Inches	Horizontal Probe (fpm)	Vertical Probe (fpm)
2	360	385
4	390	390
6	400	400
8	400	400
10	405	405
12	410	400
14	410	400
15	420	410

TABLE 15
DILUTION TUBE FLOW PROFILE - RUN 44
ENGINE STAND - STEADY-STATE OPERATION

Inches	Horizontal Probe (fpm)	Vertical Probe (fpm)
2	380	385
4	400	390
6	400	390
8	400	400
10	400	405
12	405	410
14	405	415
15	410	420

TABLE 16

DILUTION TUBE MASS PROFILE AT SAMPLING ZONE

X (In.)	Time (Min)	Traverse Net Wt. (μg)	Reference Net Wt. (μg)	Ratio
1.75	20	93	98	0.949
3.75	20	102	86	1.186
5.75	20	122	95	1.284
7.75	20	95	100	.950
9.75	20	108	112	.964
11.75	20	97	75	1.293
13.75	20	108	107	1.009
15.75	20	107	--	--
MEAN		104	96	1.075
σ		9.4	12.5	0.178
100 (σ/Mean)		9.0	13.0	16.6
1.75	20	107	113	0.947
3.75	20	121	92	1.315
4.75	20	117	104	1.125
5.75	20	103	100	1.030
7.75	20	128	115	1.113
9.975	20	123	112	1.098
10.75	20	97	--	--
11.75	20	--	111	--
13.75	20	107	128	0.836
15.75	20	110	127	0.866
MEAN		113	111	1.041
σ		10.2	11.7	0.156
100 (σ/Mean)		9.0	10.5	15.0

Note: For the purposes of statistical calculations, the (--) data were omitted because they fell out of $\pm 2\sigma$ confidence limits. As a result of these tests, we feel that the particle concentration profile of a sampling tube should be such that 100 (σ/Mean) <10.0%. The 10% deviation can be attributed to filter handling and measurement errors, variations in engine operation, and variation of diluent air conditions, such as humidity and temperature.

three separate collectors were used during a single run, and 2) a mass profile in the vertical and horizontal axis using 47 mm Gelman Type A filters at 14 liters/min at selected points sampling for 20 minutes each during a run. These data are presented in Table 16, page 96.

Comparison of collected weights in the Andersen samplers is shown by run number in Table 17.

TABLE 17
PARTICULATE MASS COLLECTED BY ANDERSEN SAMPLERS
(By Run Number)
(Engine Stand Runs)

	Andersen Samplers at 1 cfm (Grams)		
Run No.	#1	#2	#3
6	0.0427	0.0481	0.0417
12	.0999	.1032	.1006
13	.0727	.0704	.0606
14	.0402	.0419	.0396
15	.0007	.0006	.0005
16	.0077	.0088	.0053
18	.1270	.1242	.1222
20	.1141	.1029	.1122
22	.0076	.0080	.0079
31	.0312	.0411	.0372
32	.0035	.0035	.0043

Table 18 indicates mass collected by multiple 4 cfm total filters at the sampling zone.

The temperature and flow rate variations during cyclic vehicle operation are shown in Figures 20-22 and 23-25, respectively.

TABLE 18

PARTICULATE MASS COLLECTED BY 4 CFM GELMAN A FILTERS BY RUN NUMBER

	Mass Collected (gms) by 4 cfm Filters	
Run No.	Filter #1	Filter #2
47A	.1499	.1504
47C	.0690	.0695
47E	.1752	.1773
47F	.1210	.1227
48A	.0071	.0066
48B	.0060	.0061
48C	.0065	.0065
48D	.0058	.0075
48E	.0146	.0139
48F	.0054	.0056
51A	.0244	.0242
51B	.0092	.0099
51C	.0064	.0067
53A	.0080	.0068
53B	.0048	.0047
53C	.0040	.0043
58A	.0023	.0023
58B	.0009	.0011
58C	.0006	.0007
58D	.0009	.0008
58E	.0055	.0055
59	.1534	.1593
60A	.0079	.0083
60B	.0039	.0040
60C	.0028	.0028
61	.0321	.0303
62A	.0026	.0025
62B	.0015	.0015
62C	.0007	.0009
63	.0100	.0100

Figure 20

Tube Temperature Monitor at Sampling Zone. Probe Position at 8" Horizontal California 7-Mode Cycle-Cold Start

Nominal dilution tube total flow = 525 scfm

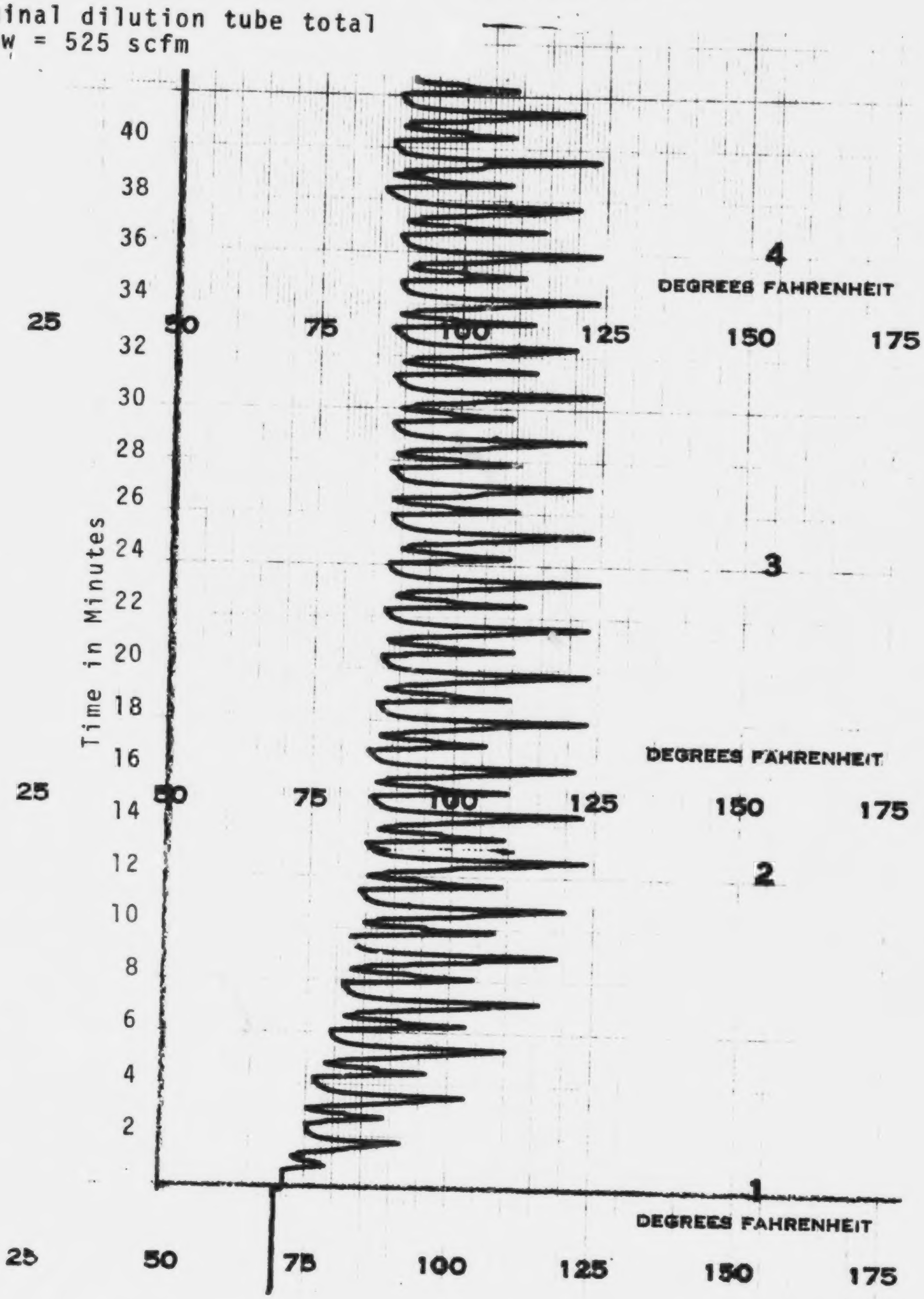
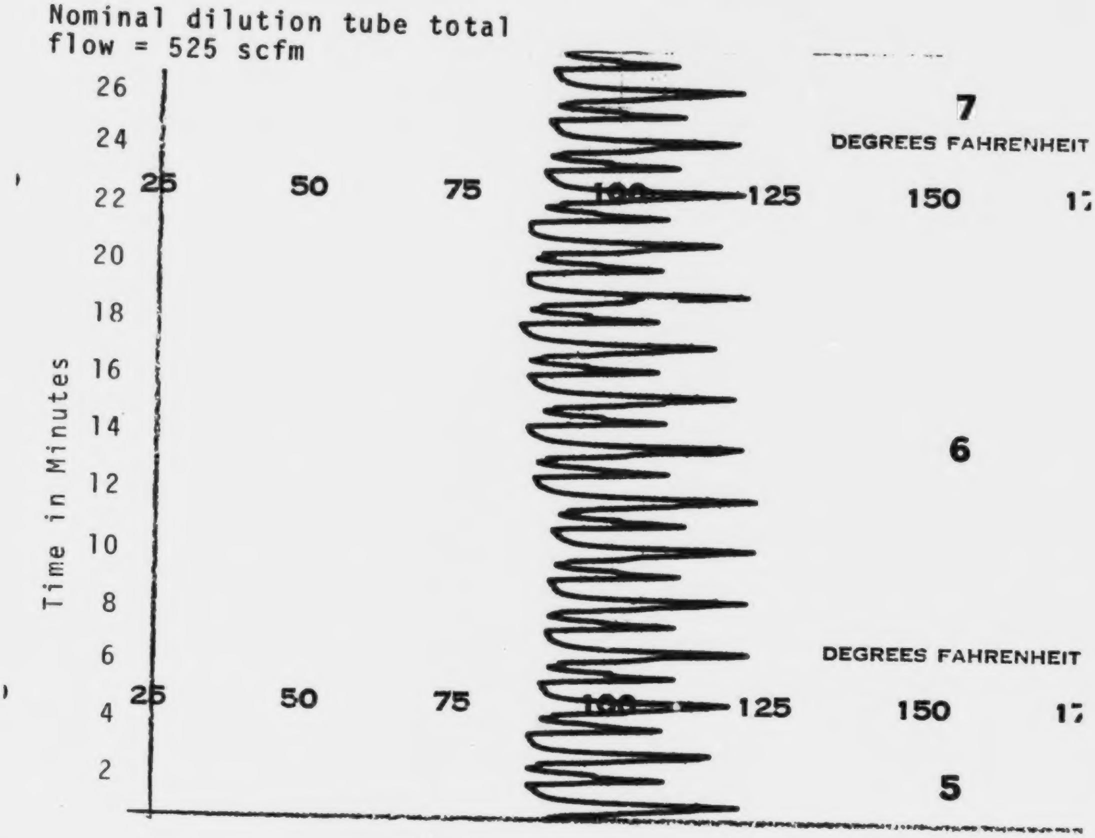


Figure 21

Tube Temperature Monitor at Sampling Zone. Probe Position at 8" Horizontal California 7-Mode Cycle-Hot Start



Temperature, °F

Figure 22

Tube Temperature Monitor at Sampling Zone. Probe Position at 8" horizontal
Federal Cycle (LA-4) - Hot Start

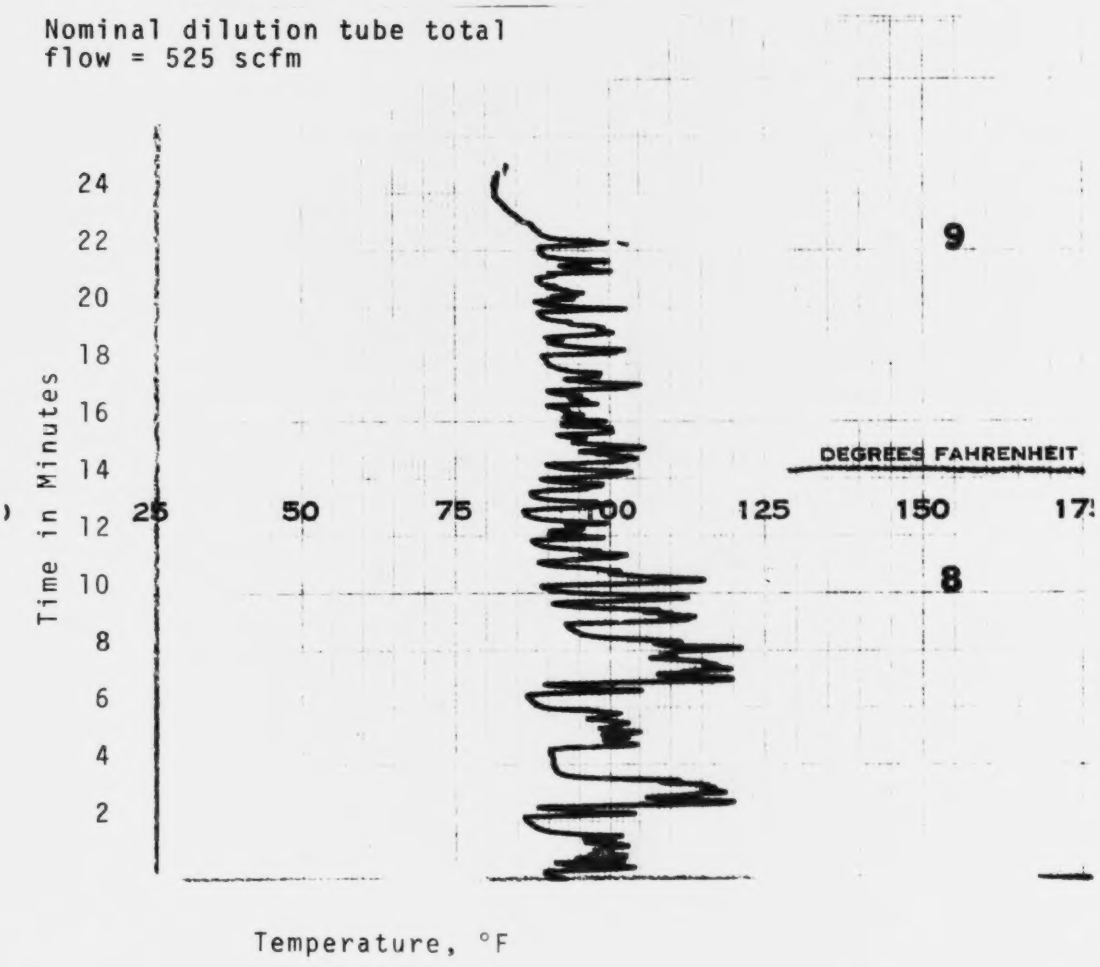


Figure 23

Dilution Tube Flow Monitor at Sampling Zone. Probe Position at 8" Horizontal California 7-Mode Cycle-Hot Start

Nominal dilution tube total flow = 525 scfm

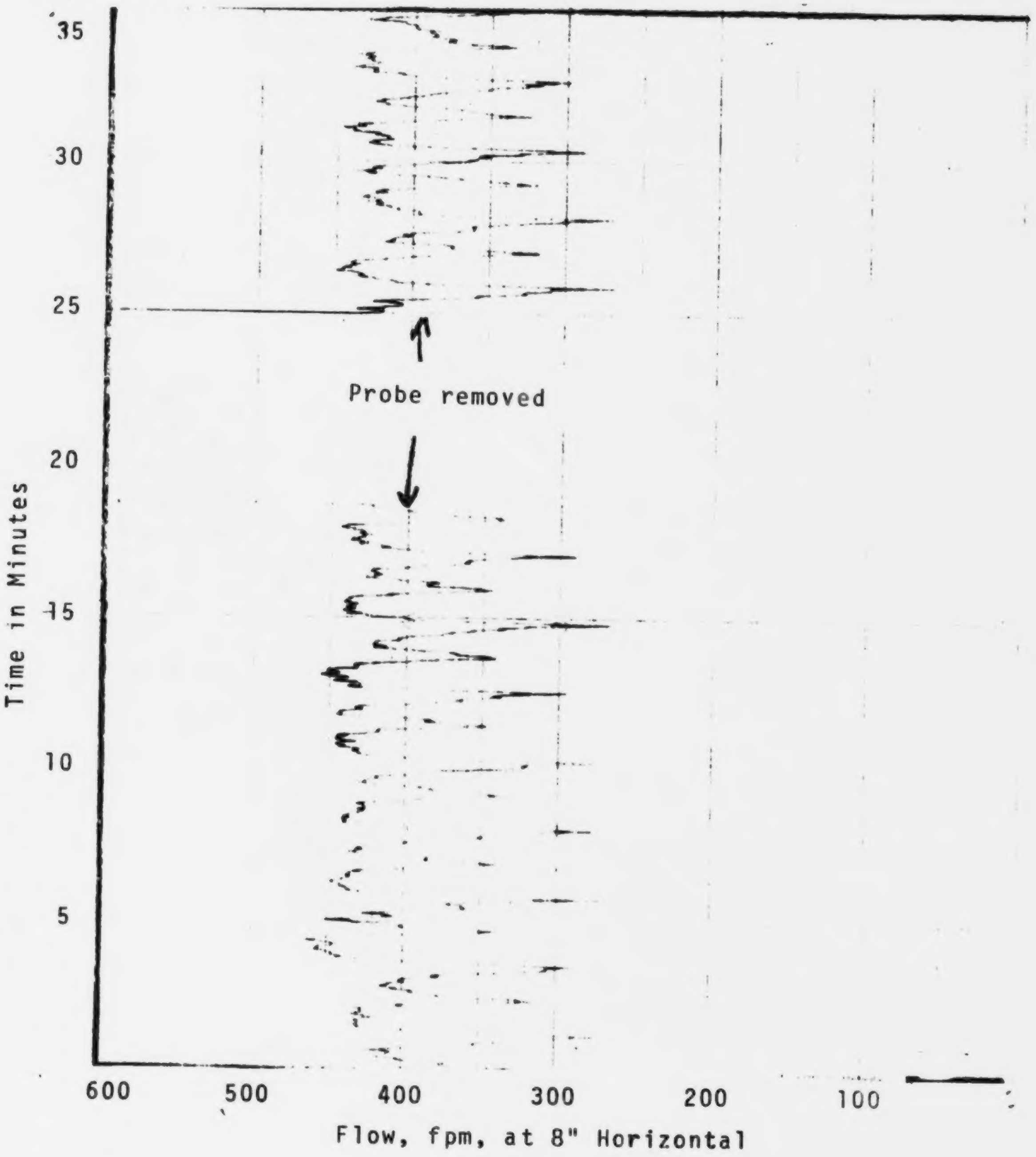


Figure 24

Dilution Tube Flow Monitor at Sampling Zone. Probe Position at 8" Horizontal California 7-Mode Cycle-Cold Start

Nominal dilution tube total flow = 525 scfm

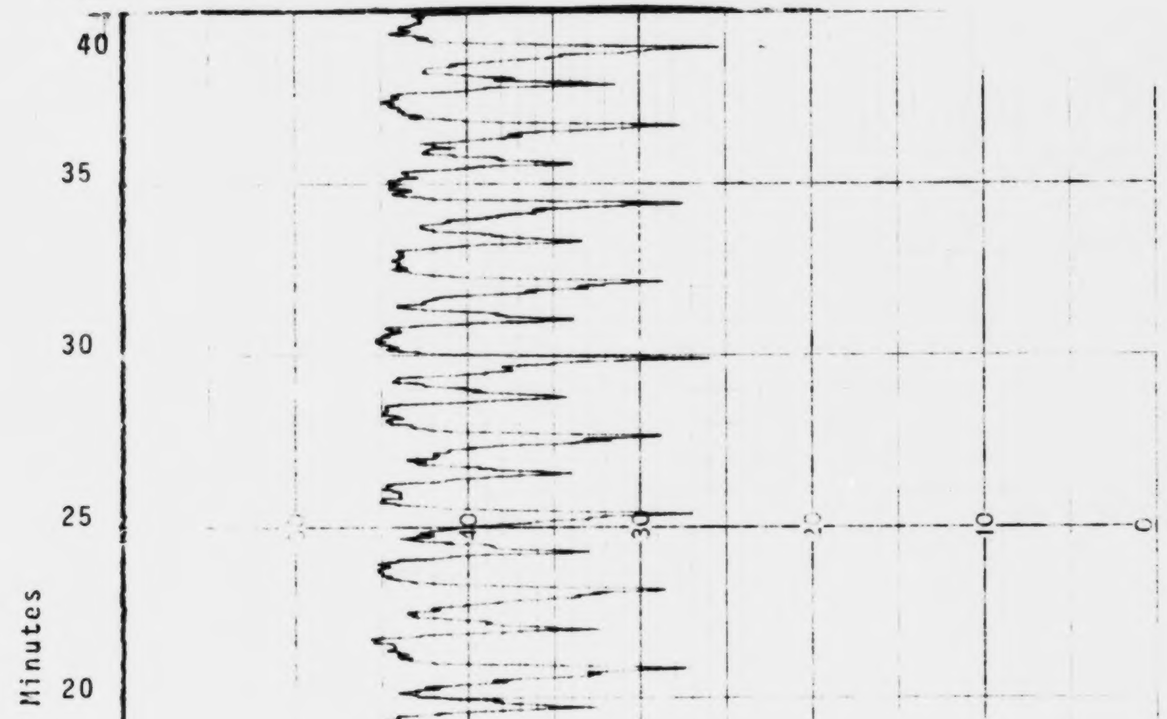
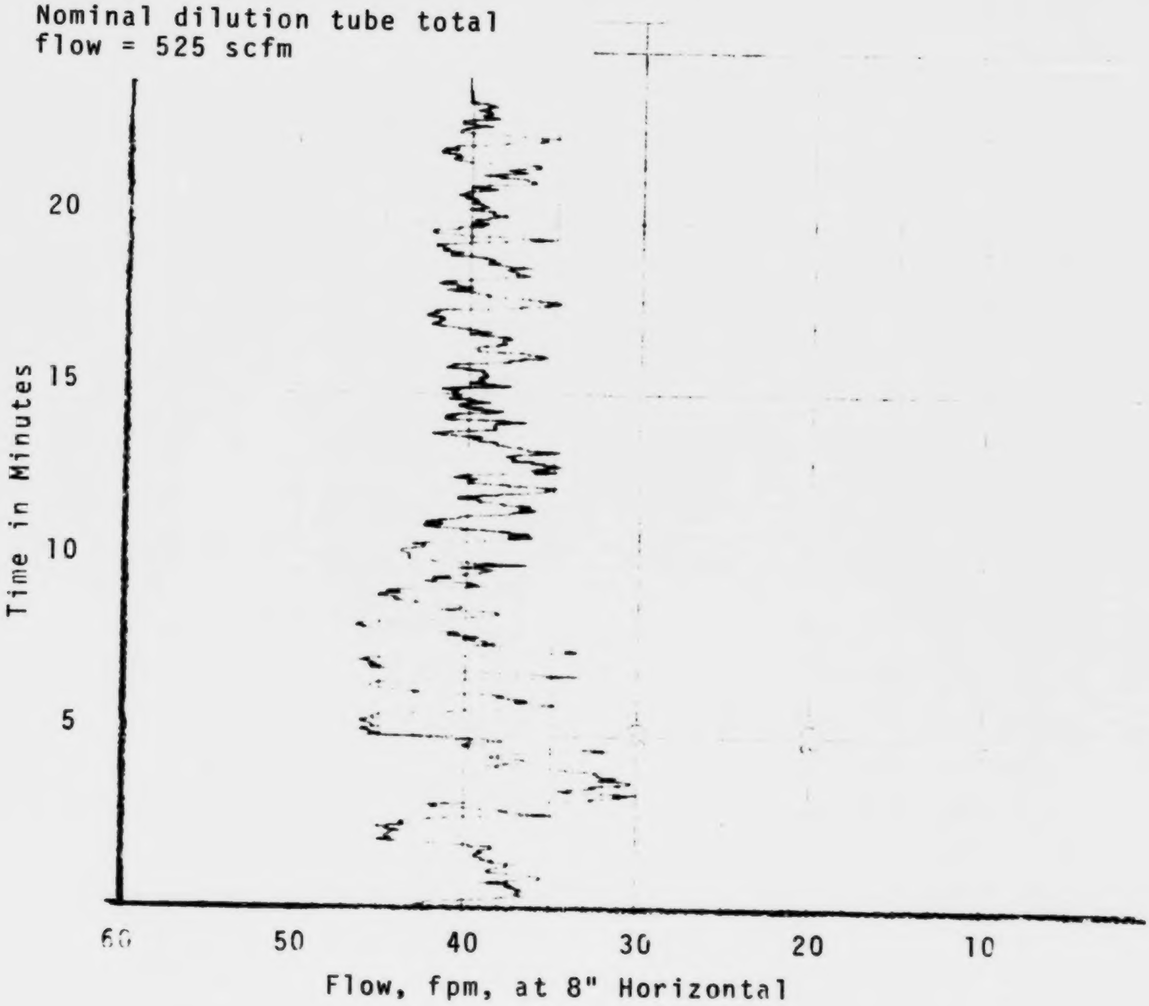


Figure 25

Dilution Tube Flow Monitor at
Sampling Zone. Probe Position
at 8" Horizontal
Federal Cycle (LA-4) - Hot Start



D. TEST FUELS AND OILS

1. Physical Properties

The physical properties of each test fuel used in this study is shown in Table 19. Sufficient fuel of each type was obtained for the anticipated total requirement. Additional analysis was not conducted unless an additional shipment was received.

Similarly, trace metal analysis was conducted for each test fuel; this data is presented in Table 20.

The physical properties of the engine oils used in this study and the run number relationships are shown in Table 21.

TABLE 21

ENGINE OIL PHYSICAL PROPERTIES
AMOCO SAE 30

Property	AMOCO 100	AMOCO 200
Gravity, °API	26.4	27.1
Flash, °F	450.0	495.0
Pour, °F	0	-5
Viscosity, °F, SUS, ext.	75,000	80,000
Viscosity, 100°F, SUS	555	568
Viscosity, 210°F, SUS	66	66
Viscosity index	95	94
Color ASTM	5	4.5
Sulfated ash, % wt.	1.0	0.5
Carbon residue, % wt.	1.3	-
API classification	MS-DM	MS-DM
Used in	Runs 3-18	Runs 19-67

The trace metal analysis of these oils, both new and after selected test runs are shown in Tables 22 and 23.

TABLE 19
PHYSICAL ANALYSIS OF TEST FUELS

Distillation D86 °F	IND HO	IND HO-15	IND§ HO-30*	IND HO 3cc TEL/gal	IND HO-30**	AMOCO 91 RON	AMOCO 91 RON 0.5 TEL	IND HO-30	IND M.F.§ 91 RON
IBP	100	88	92	90	90	93	93	96	90
5	126	118	118	116	118	119	114	120	116
10	140	137	132	130	133	129	125	134	127
20	165	166	162	159	162	150	146	161	150
30	190	190	190	190	188	169	169	185	171
40	207	207	207	202	208	188	191	205	190
50	221	220	218	220	222	204	211	220	209
60	231	236	238	235	234	219	230	232	223
70	244	249	250	249	249	234	252	246	239
80	268	272	274	274	273	258	281	268	-
90	320	332	326	328	320	294	312	314	304
95	368	386	364	370	368	329	358	344	347
EP	395	398	404	394	394	372	386	385	379
% Recovery	96.5	96.0	97.0	97.0	96.5	98.5	98.0	98.5	98.0
% Residue	0.6	0.6	0.6	0.4	0.5	0.2	0.4	0.1	0.4
% Loss	2.9	3.4	2.4	3.6	3.0	1.3	1.6	1.4	1.6
RVP	7.3	7.4	8.2	8.5	--	8.8	9.7	8.8	9.1
Octanes:									
MON	87.5	92.3	96.3	95.6	95.9	82.7	82.5	95.6	82.6
RON	97.4	101.2	103.4	103.2	102.9	91.0	90.9	102.9	91.2
FIA:									
% Saturates	66.4	63.1	65.9	65.1	68.1	73.0	70.2	71.7	70.6
% Olefins	4.2	4.6	3.6	3.2	3.0	5.4	8.2	4.9	8.1
% Aromatics	29.4	32.3	30.5	31.7	28.9	21.6	21.6	23.4	21.3
TEL (cc/gal)	0.06	1.5	3.0	3.0	3.0	0	0.43	2.86	0

Distillation D86 °F	AMOCO IND 0	AMOCO 0.5 TEL 91.6 RON	AMOCO No TEL + AMOTONE 91 RON	IND M.F. No TEL 91 RON 15214	IND M.F. 0.5 TEL 91 RON 15218	FUEL B No TEL 91.7 RON	FUEL A Car Pool Fuel 96.8 RON	FUEL C No TEL 91.5 RON
IBP	78	74	70	112	88	70	86	88
5	100	90	80	118	102	110	112	110
10	112	102	90	124	107	122	125	123
20	140	120	110	140	112	152	151	148
30	170	148	122	160	130	184	180	174
40	184	168	138	180	160	210	204	199
50	210	168	138	180	160	210	222	218
60	224	210	196	220	220	250	242	230
70	240	236	222	240	240	280	204	259
80	269	260	256	254	260	304	302	296
90	330	300	302	290	300	350	360	370
95	349	340	360	328	350	398	-	420
EP	358	360	370	372	370	400	392	443
% Recovery	96.0	97.0	96.0	99.0	98.0	94.0	93.5	97.0
% Residue	0.3	0.5	0.3	0.4	0.4	0.5	0.4	0.7
% Loss	3.7	2.5	3.7	0.6	1.6	5.5	6.1	2.3
RVP	8.7	8.4	11.2	-	-	-	10.4	9.0
Octanes:								
MON	84.0	84.2	84.0	83.4	91.0	83.1	89.4	83.6
RON	91.0	91.6	91.0	91.4	99.2	91.7	95.8	91.5
FIA:								
% Saturates	73.0	70.0	71.0	69.7	68.5	64.2	75.7	71.4
% Olefins	5.7	8.8	6.1	7.4	4.2	5.8	4.6	4.0
% Aromatics	21.3	21.2	22.9	22.9	27.3	30.0	19.7	24.6
TEL (cc/gal)	0.2	0.56	0	0	0.47	0.03	2.66	0.266

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*First lead Indolene HO-30 Fuel
**Second lead Indolene HO-30 Fuel (Runs 11 through 17)
§IND = Indolene
§M.F. = Motor Fuel

Fuels A, B, C - Commercial fuels

TABLE 20

TEST FUEL TRACE METALS CONTENT

(Wt. %)

Fuel Ref.	Fe	Ni	Cu	Al	Ca	Si	Mg	Mn	Cr	Sn	Zn	Ti	Sb	C	H
Indolene HO 30	<.0001	<.00005	<.00002	<.0001	<.0001	<.0001	<.0001	<.00005	<.0001	<.0001	<.0003	<.0001	--	86.35	13.09
Indolene HO 0	.033	<.0001	.00005	<.0001	<.0001	.0003	.0002	.0002	<.0001	.0002	.0007	<.0001	<.00005	86.25	13.09
Indolene HO-30	.0012	<.00005	<.00003	<.00005	<.0001	<.0001	<.00005	<.00003	<.00005	<.00005	<.0001	<.00005	<.00005	82.3	12.60
Indolene O 91 Oct	.00009	<.00005	<.00003	<.00005	<.0001	<.0001	<.00005	<.00003	<.00005	<.00005	<.0001	<.00005	<.00005	82.3	13.09
AMOCO No Pb	.00005	<.00005	<.00003	<.00005	<.0001	<.0001	<.00005	<.00003	<.00005	<.00005	<.0001	<.00005	<.00005	84.6	13.45
AMOCO 0.5 Pb	.00009	<.00005	<.00003	<.00005	<.0001	<.0001	<.00005	<.00003	<.00005	<.00005	<.0001	<.00005	<.00005	83.5	12.96
AMOCO*0.5 Pb	<.00005	<.00005	<.00003	.0004	<.0001	<.0001	<.00005	<.00003	<.00005	<.00005	<.0001	<.00005	<.00005	85.60	13.4
AMOCO AMOTONE	<.00005	<.00005	<.00003	.0006	<.0001	<.0001	<.00005	<.00003	<.00005	<.00005	<.0001	<.00005	<.00005	85.70	13.4
Fuel Type B No Pb	<.00005	<.00005	<.00003	.0002	.0001	<.0001	<.00007	<.00003	<.00005	<.00005	<.0001	<.00005	<.00005	86.20	12.7
Fuel Type A	<.00005	<.00005	<.00003	<.00005	<.0001	<.0001	<.00005	<.00003	<.00005	<.00005	<.0001	<.00005	<.00005	85.48	14.30
Indolene* O 91 Oct	.0001	<.00005	<.00003	.0006	<.0001	<.0001	<.00005	<.00003	<.00005	<.00005	<.0001	<.00005	<.00005	85.6	13.7
Indolene Motor Fuel 0.5 Pb	<.000025	<.000025	<.000003	<.000025	<.000025	--	<.000025	<.000005	<.000025	<.000025	<.00007	<.000025	--	85.56	13.22
Indolene Motor Fuel No Pb	<.000025	<.000025	<.000003	<.000025	<.000025	--	<.000025	<.000005	<.000025	<.000025	<.00007	<.000025	--	85.69	13.45

*Different shipments

TABLE 22
TRACE METAL ANALYSIS OF NEW ENGINE OIL

Element	AMOCO 100	AMOCO 200
Fe	.0002 wt. %	.0003 wt. %
Ni	<.0001	<.0003
Cu	<.00002	<.0001
Al	.0001	<.0003
Ca	.0017	.0005
Si	.0001	-
Mg	.089	.11
Mn	.0001	<.0001
Pb	.0006	<.0005
Cr	<.0001	<.0003
Sn	<.0001	<.0003
Zn	.081	.10
Ti	<.0001	<.0003
P	.05	-
Mo	<.0001	-

E. COMBUSTION CHAMBER DEPOSITS

Combustion chamber deposits have been collected, weighed, and analyzed for major elements; and, in selected cases for trace elements. These data have been collected only on the engine dynamometer studies; however, Table 24 indicates deposit weights by run number. Table 25 shows major elemental analysis and Table 26 trace metal analysis.

F. EXHAUST GASES

Total unburned hydrocarbons, saturated hydrocarbons, carbon monoxide, and nitric oxide gaseous exhaust emissions have been determined during each engine dynamometer study. The fuel and fuel additions were found to have significant effects on such emissions during the

TABLE 23

USED ENGINE OIL TRACE METAL ANALYSIS
(Weight Percent)

Element	Run 5 Oil Filter	Run 13 Oil Filter	Run 13 Crankcase	Run 23 Crankcase	Run 29 Crankcase	Run 31 Crankcase	Run 43 Crankcase	Run 44 Crankcase
Fe	.012	.012	.012	.012	.0053	.0057	.0053	.0033
Ni	<.0005	<.0005	<.0005	<.0005	.0002	<.0005	<.0002	<.0002
Cu	.0003	.0002	.0002	.0003	.0003	.0003	.0003	.000
Al	<.0005	.0013	.0012	.0012	.0006	.0009	.0003	.0005
Ca	.0057	.0028	.0026	.0012	.0015	.0008	.0021	.0027
Si	<.0005	.0010	.0030	.0026	.0019	.0028	.0007	.0004
Mg	.083	.084	.088	.12	.13	.12	.096	.11
Mn	<.0005	<.0005	<.0005	.0005	.0003	.0005	.0002	.0002
Pb	.12	1.3	1.3	1.1	.018	.91	.12	.055
Cr	.0008	.0055	.0048	.0009	<.0002	<.0005	<.0002	<.0002
Sn	<.0005	<.0005	<.0005	<.0005	.0007	.0005	<.0002	<.0002
Zn	.078	.082	.076	.092	.084	.098	.078	.088
Ti	<.0005	<.0005	<.0005	<.0005	<.0002	<.0005	<.0002	<.0002
P	<.1	<.3	<.3	-	-	.029	.064	.074
Mo	<.0001	.0012	.0011	-	-	-	.0003	.0003

TABLE 24
COMBUSTION CHAMBER DEPOSITS

Run No.	Engine Operation (Hours)	Deposit (Weight in Grams) 4 Left Cylinders	4 Right Cylinders	Total
3	103.7	61.235	54.418	115.653
4	128.8	73.846	69.200	143.046
5	126.1	9.7744	9.3032	19.0776
6	127.0	49.9348	45.8379	95.7727
7	126.1	44.056	43.280	87.330
8	128.9	69.230	66.130	135.360
9	127.3	97.930	75.790	173.720
11 12	179.5	93.98	91.48	185.46
13 14	139.7	55.30	64.70	139.00
16 17	180.2	11.80	10.05	21.85
18	132.6	94.69	94.60	188.85
19	123.1	77.35	54.41	131.76
20	124.1	59.53	45.25	104.78
21	125.1	25.50	20.00	45.50
22	125.5	8.47	7.03	15.50
23	123.5	85.54	74.98	160.52
29	122.6	14.58	15.78	30.36
31	123.6	61.60	66.23	127.83
32	124.0	18.56	21.39	39.95
40	123.0	18.73	21.75	40.48
44	131.2	17.22	18.80	36.02
59	100.0	23.32	23.62	46.94

TABLE 25
COMBUSTION CHAMBER DEPOSIT ANALYSIS

Run No.	Weight Percent Pb	Fe	C	Br	Cl
4	64.6	0.26	5.7	8.21	10.81
5	5.9	1.10	55.9	0.55	0.57
6	54.9	0.27	12.0	8.19	9.78
7	72.0	0.2	11.0	0.6	0.28
8	59.8	0.18	7.8	20.67	0.58
9	67.9	0.217	7.4	0.55	13.55
12 13 }	66.4	0.177	6.01	9.10	8.99
14	65.6	0.190	6.08	9.12	9.85
16 17 }	4.44	0.587	55.0	0.19	0.40
18	62.1	0.240	6.5	8.03	8.41
19	64.4	0.076	5.2	7.42	11.48
20	64.9	0.186	4.8	8.14	12.11
21	40.0	0.38	25.7	3.68	3.37
22	4.92	0.779	49.3	0.24	0.37
23	65.0	0.108	4.7	6.92	11.08
29	<0.7	0.23	52.9	0.94	3.10
31	48.7	0.31	14.4	6.3	11.2
40	32.0	0.18	-	-	-
44	4.0	0.20	-	-	-
59	43.7	0.71	23.2	1.63	3.35

TABLE 26

ENGINE COMBUSTION CHAMBER DEPOSITS - TRACE METALS

(Wt. %)

Run No.	Ni	Cu	Al	Ca	Si	Mg	Mn	Cr	Sn	Zn	Ti
17	<0.010	0.038	0.44	0.075	0.069	1.60	0.013	0.046	0.049	2.10	<0.010
18	<0.010	0.005	0.33	0.016	0.056	0.27	0.007	0.023	<0.010	0.25	<0.010
19	<0.010	0.007	0.10	<0.010	0.045	0.12	<0.005	0.014	<0.010	0.069	<0.010
20	<0.010	0.009	0.41	<0.010	0.12	0.13	0.015	0.030	<0.010	0.064	<0.010
21	<0.010	0.051	0.12	0.024	0.066	1.30	0.009	0.013	<0.010	0.79	<0.010
22	<0.010	0.075	0.17	0.054	0.065	3.30	0.012	0.012	<0.010	1.8	<0.010
23	<0.010	0.005	0.028	0.014	0.062	0.73	<0.005	0.007	<0.010	0.32	<0.010
29	0.0002	0.0003	0.0006	0.0015	0.0019	0.130	0.0003	<0.0002	0.0007	0.084	<0.0002
31	<0.010	0.012	0.034	0.019	0.10	0.58	<0.005	<0.010	<0.010	0.35	<0.010
40	<0.010	0.040	0.110	0.027	0.027	0.88	0.006	<0.010	<0.010	0.70	<0.010
44	<0.010	0.022	0.230	0.046	0.013	0.64	0.007	<0.010	<0.010	0.73	<0.010

75-hour engine stabilization sequence. Figures 26, 27, and 28 indicate the percentage change in these emissions, as an average of all five (5) conditioning cycles, from 0 engine hours to 75 engine hours.

Graphical representation of actual hydrocarbon emissions during the conditioning sequence, sampling sequence, and cruise mode vehicle studies are shown in Appendix A.

The level of aldehydes present in a cold trap condensate of exhaust gas sample and determined polarographically is shown in Table 27.

TABLE 27
EXHAUST GAS CONDENSATE ALDEHYDES

Run No.	Mode	Aldehydes (ppm of Collected Condensate)
56	2250 rpm:	
	Before catalyst	590 ppm HCHO
	After catalyst	290 ppm HCHO

G. PARTICULATE

1 Mass Emission Rates

Total particulate mass emission levels by run number are shown in Tables 28 and 29. The mass emission rates are presented in grams/mile and include all emitted particulate unless otherwise noted. Additionally, the mass emission rates are shown by sampling technique, i.e. Andersen-Filter at 1 cfm, single Gelman A glass fiber filter at 4 cfm, etc.

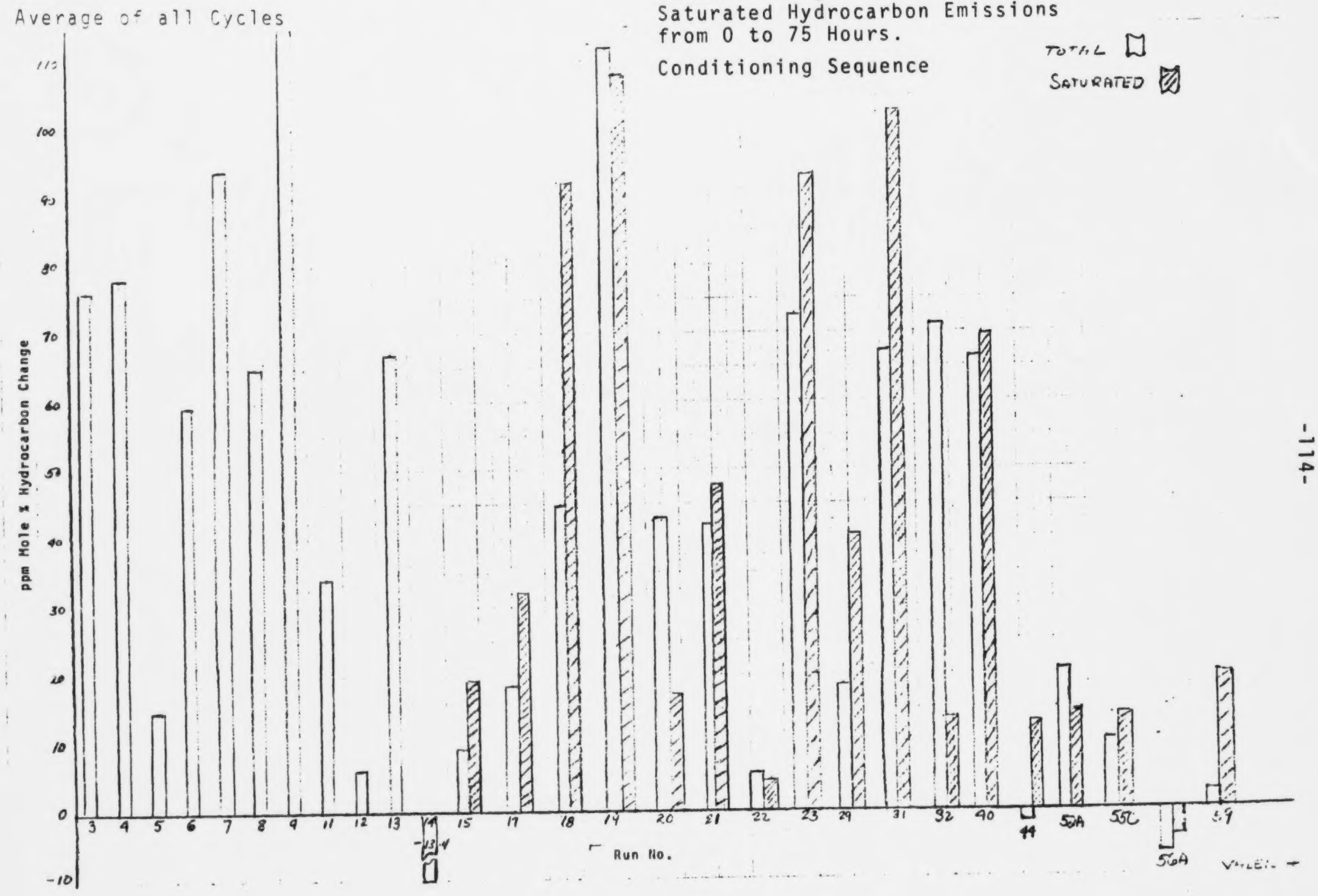
2. Mass Distribution

Table 30 indicates the mass medium equivalent diameter of emitted particles for the runs indicated. These data are based on dilution tube and Andersen sampler samples. The cumulative mass distribution curves from which these values are obtained are contained in Appendix B.

Figure 26

Percent Change in Total and Saturated Hydrocarbon Emissions from 0 to 75 Hours.

Conditioning Sequence



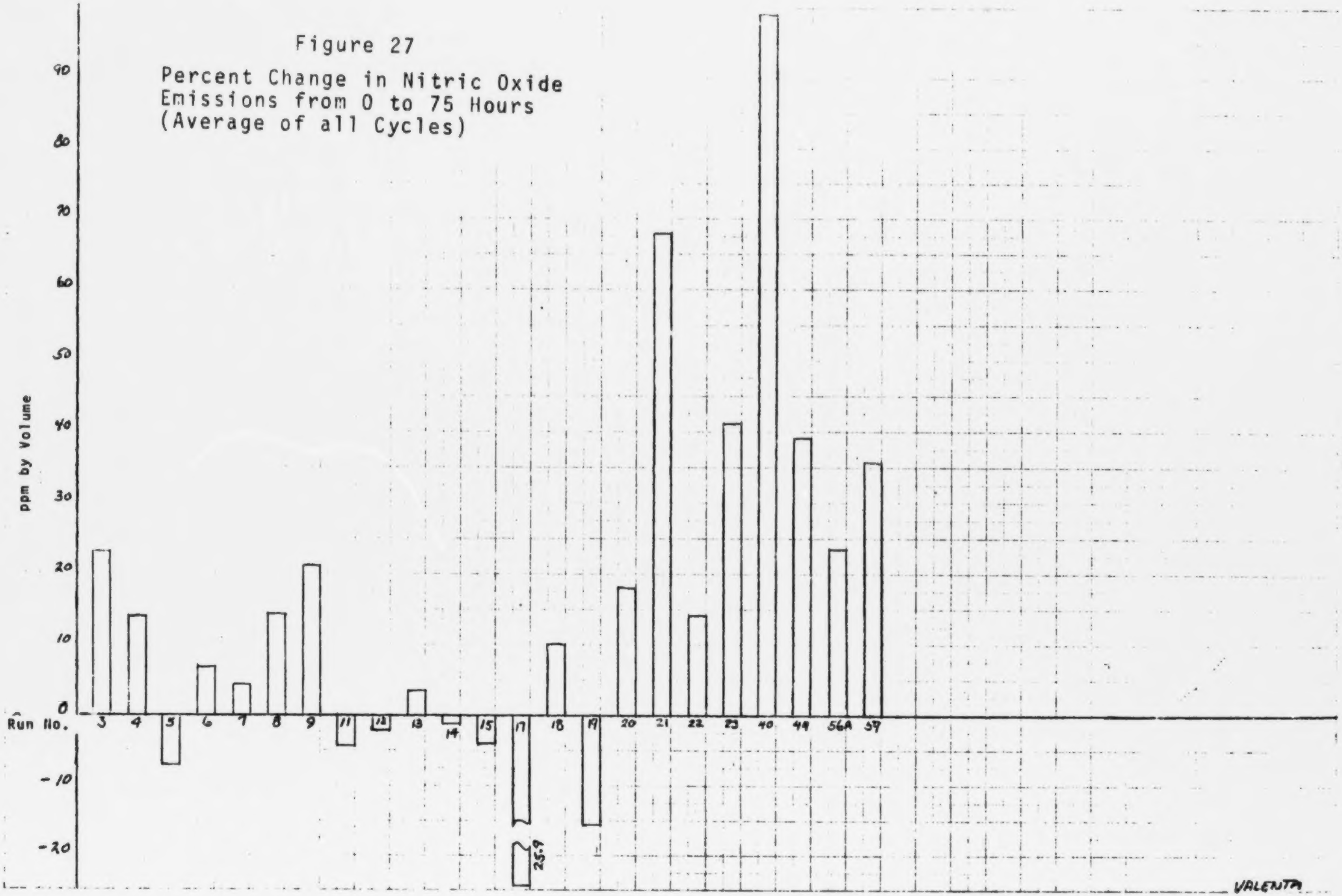


Figure 27

Percent Change in Nitric Oxide Emissions from 0 to 75 Hours (Average of all Cycles)

Figure 28

Percent Change in Carbon Monoxide Emissions from 0 to 75 Hours Conditioning Sequence and Cruise Modes

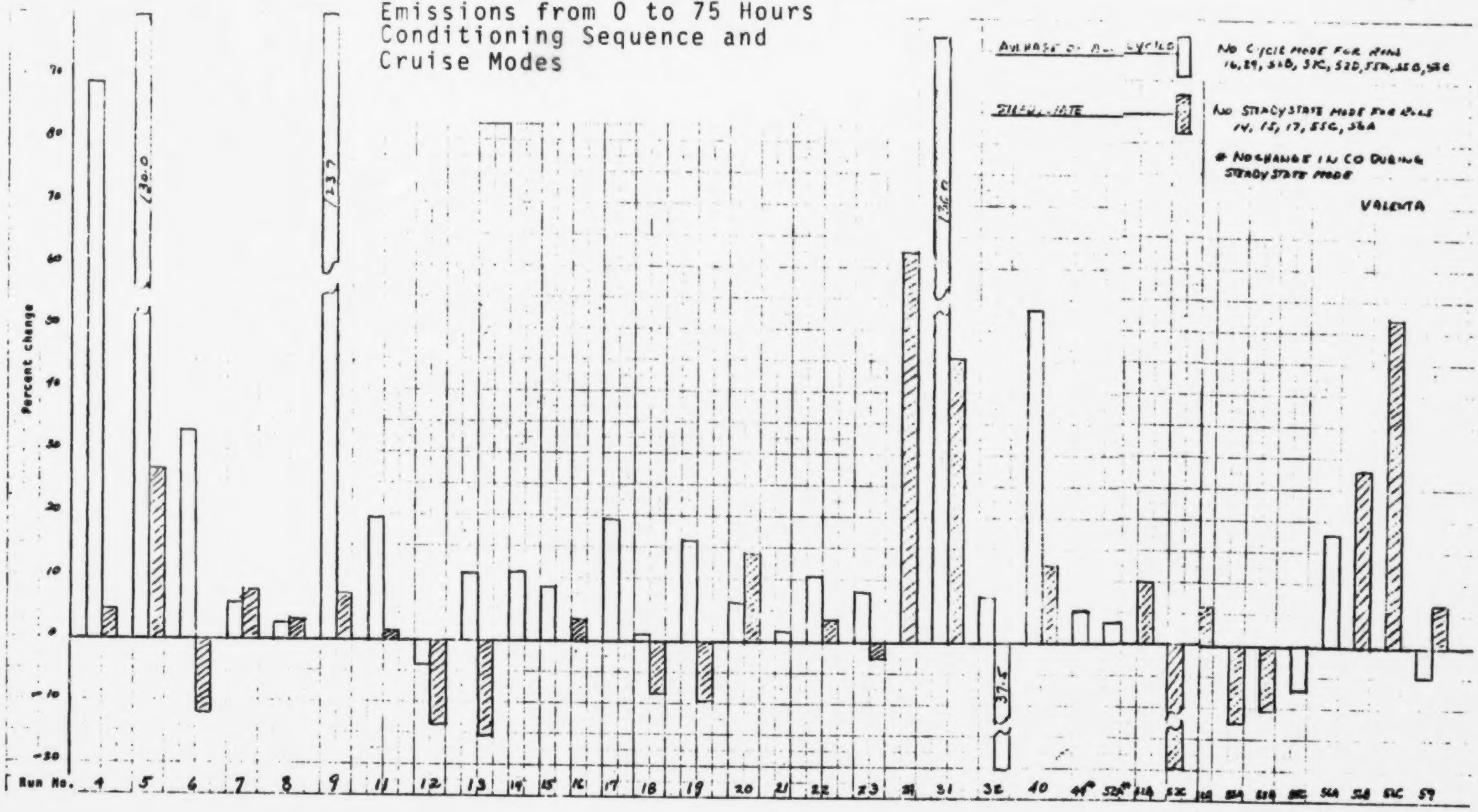


TABLE 28

ENGINE STAND RUNS - PARTICULATE MASS EMISSIONS

(Emissions Grams per Mile)

Run No.	Mode	Dilution Tube	Andersen	Back-up 1 cfm	= Total	4 cfm Filter***	Other
3	SS - 60 mph	-	0.02751	-	0.02751		
4	↓	0.000598	.03734	0.068436	.109040		
5		.000762	.000481	.002675	.002987		
6*		-	.000659	.002986	.003645		
6		.002242	.014860	.013297	.030399		
7*		-	.001145	.004722	.005868		
7		.006015	.024635	.131804	.162455		
8		.017426	.064896	.073328	.155641		
9		.008622	.033991	.035797	.07841		
11		.007324	.039996	.069925	.117246		
12	Dow Cycle	.007833	.043608	.078990	.130431		
13	SS - 60 mph	.012634	.039670	.083688	.135999		
14	Dow Cycle	.004030	.031209	.105388	.140629		
15*	SS - 60 mph	-	.000072	.002366	.002438		
16	SS - 60 mph	.002962	.002792	.010515	.016267		
17	Dow Cycle	.001693	.003677	.005048	.010419		
18	SS - 60 mph	.006700	.043537	.096835	.147074		
19	↓	.006407	.033556	.052133	.092097		
20		.006683	.037601	.049195	.093480		
21		.000642	.004858	.013223	.018724		
22		.001944	.002636	.008561	.013241		
23		.001944	.029578	.056243	.091014		
29		.00085	.00169	.00055	.00310		0.0026 THF
31		.00905	.01247	.04321	.06474	0.0670	.0499 THF
32		.00063	.00114	.00141	.00320	.0015	
40		.00056	.00452	.00631	.01141	.0126	
44		.00076	.00235	.01100	.01412	.0135	
52R		.0005	.0152	.0155	.0312	.0308	
52R	SS - 30 mph	.0001	.0405	.0011	.0417	.0406	
52L	SS - 60 mph	.0001	.0344	.0016	.0361	.0361	
52L	SS - 30 mph	.0005	.0186	.0083	.0274	.0269	
55**	SS - 60 mph	.0003	.0127	.1038	.1168	.1205	
55**	SS - 30 mph	.00015	.0105	.0383	.0489	.0737	
55**	Dow Cycle	.0007	.0156	.0713	.0876	.0978	
56C	SS - 60 mph	.00152	.0032	.0259	.03064		
59	SS - 60 mph	.00035	.00319	.0235	.0271	.0135	

Code: SS = Steady State
THF = Total Hot Filter
* = Blank dilution air only
R = Rich Carburetor Mix
L = Lean Carburetor Mix
** = Platinum Muffler
*** = 142 mm Gelman Type A glass fiber filter operating at 4 cfm flow

TABLE 29

CHASSIS DYNAMOMETER
(Emissions Grams per Mile)

Run No.	Mode	Vehicle Mileage	Dilution Tube	Andersen	Back-up 1 cfm	Total	4 cfm Filter	Other
24	SS - 60 mph	10,000	0.0059	0.0364	0.0817	0.1241	0.1160	
25	SS - 60 mph	10,360	.0051	.0357	.0738	.1147	.0935	
27	SS - 60 mph	7,900	.0004	.0343	.0668	.1064	.0855	
28	SS - 60 mph	8,260	.0016	.0433	.0746	.1196	.1054	{ .109*** .079****
30	HS FTP	19,000	-	-	-	-	.1558	{ .101*** .078****
33	SS - 60 mph	500	.0000	.0010	.0108	.0119	.0032	
34	SS - 60 mph	30,000	.0302	.0355	.1357	.2015	.1760	
35A	CS FTP	30,400	-	-	-	-	.5795	
35B	HS FTP	-	-	-	-	-	.4014	
35C	HS FTP	-	-	-	-	-	.5761	
36*A	CS FTP	700	-	-	-	-	.2019	
36*B	SS - 60 mph	-	-	-	-	-	.0162	
37	SS - 60 mph	12,885	.0007	.0279	.1069	.1355	.0849	
38	SS - 60 mph	35,000	.0005	.0286	.1007	.1299	.0896	
39C	CS FTP	500	-	-	-	-	.0059	
39A	HS FTP	-	-	-	-	-	.0119	
39B	HS FTP	-	-	-	-	-	.0144	
39D	HS FTP	-	-	-	-	-	.0068	
39E	HS FTP	-	-	-	-	-	.0102	
41	SS - 60 mph	600	.0000	.0014	.0392	.0408	.0446	
42A	CS FTP	53,000	-	-	-	.0097		
42B	HS FTP	53,000	-	-	-	.0093		
42C	SS - 60 mph	53,000	.0005	.0007	.0075	.0088	.0037	
43	SS - 60 mph	2,500	.0002	.0018	.0094	.0115	.0588	
45	SS - 60 mph	3,000	.0001	.0042	.0182	.0225	.0106	
46	CS FTP	3,770	-	-	-	-	.0507	
46	CS FTP	-	-	-	-	-	.0409	
46	CS FTP	-	-	-	-	-	.0426	
46	CS FTP	-	-	-	-	-	.0400	
46	HS FTP	-	-	-	-	-	.0362	
46	HS FTP	-	-	-	-	-	.0477	
46	HS FTP	-	-	-	-	-	.0400	

TABLE 29 (Contd.)

Run No.	Mode	Vehicle Mileage	Dilution Tube	Andersen	Back-up 1 cfm	=	Total	4 cfm Filter
46H	HS FTP	-	-	-	-		-	.0353
48C	CS FTP	4,250	-	-	-		-	.0554
48**E	CS FTP	-	-	-	-		-	.1214
48**A	HS FTP	-	-	-	-		-	.0583
48**B	HS FTP	-	-	-	-		-	.0443
48**D	HS FTP	-	-	-	-		-	.0566
48**FF	HS FTP	-	-	-	-		-	.0468
49A	CS FTP	5,000	-	-	-		-	.0911
49B	HS FTP	-	-	-	-		-	.0519
49C	HS FTP	-	-	-	-		-	.0639
50	SS - 60 mph	3,000	.0029	.0447	.1086		.1565	.1189
51A	CS FTP	3,400	-	-	-		-	.2071
51B	HS FTP	-	-	-	-		-	.0813
51C	HS LA4	-	-	-	-		-	.1091
53A	CS FTP	13,000	-	-	-		-	.0617
53B	HS FTP	-	-	-	-		-	.0404
53C	HS LA4	-	-	-	-		-	.0708
54	SS - 60 mph	13,100	.0000	.0006	.0200		.0206	.0089
58A	CS FTP	10,000	-	-	-		-	.0196
58B	HS FTP	-	-	-	-		-	.0085
58C	HS LA4	-	-	-	-		-	.0108
58E	SS - 60 mph	-	.0002	.0060	.0100		.0162	.0020
60A	CS FTP	9,101	-	-	-		-	.0690
60B	HS FTP	-	-	-	-		-	.0336
60C	HS LA4	-	-	-	-		-	.0466
61	SS - 60 mph	-	.0026	.0039	.0128		.0193	.0113
62A	CS FTP	17,750	-	-	-		-	.0217
62B	HS FTP	-	-	-	-		-	.0127
62C	HS LA4	-	-	-	-		-	.0068
63	SS - 60 mph	-	.0001	.0027	.0065		.0093	.0036
65	SS - 60 mph	-	-	-	.0001		.0001	.0004
66A	CS FTP	9,286	-	-	-		-	.1742
66B	HS FTP	-	-	-	-		-	.0988
66C	HS LA4	-	-	-	-		-	.0605
67	SS - 60 mph	-	.0040	.0485	.1005		.1530	.1202

Code:
*Temperature = 15°F
**Temperature = 20°F
***Beta-Gauge
****Thermo-Systems, Inc., mass monitor

CS = Cold Start
FTP = California 7 Mode
LA4 = Federal 23 Mode

HS = Hot Start
SS = Steady State

TABLE 30

MASS MEDIUM EQUIVALENT DIAMETER EXHAUST PARTICULATE

Run No.	RPM	Engine (E) Vehicle (V)	MMED	Pb MMED
4		E	0.10	
6		E	1.5	
7		E	<<0.10	
8		E	0.65	
9		E	1.1	
11		E	~0.10	
12		E	~0.10	
13		E	~0.10	
14		E	<0.10	
15		E	<<0.10	
16		E	<0.10	
17		E	0.7	
18		E	0.13	
19		E	<0.10	
20		E	~0.10	
21		E	<<0.10	
22		E	<0.10	
23		E	<0.10	
24		V	<<0.10	
25		V	<0.10	
27		V	<0.10	
28		V	<0.10	
29		E	<0.10	
31		E	<0.10	
32		E	1.0	
33		V	<<0.10	
34		V	0.29	
37		V	<0.10	
38		V	<0.10	
40		E	0.37	
41		V	<<0.10**	
42		V	<0.10**	
43		V	<0.10	
44		E	<0.10	
45		V	<0.10	
47	1200	E	~0.10	<0.10
47	2250	E	<0.10	<0.10
50		V	<0.10	
52	2250	E	1.42****	
52	2250	E	0.50***	
52	1200	E	3.20****	
52	1200	E	3.20***	
54		V	<0.10	
55	2250	E	<<0.10*	
55	1200	E	<0.10	
55	Dow Cycle	E	<<0.10	
56	2250	E	0.42**	
56	1200	E	<<0.10**	

Code:

< = Less than
<< = Much less
~ = Approximately

*Platinum muffler
**Proprietary catalyst muffler
***Lean carburetor mix
****Rich carburetor mix

3. Major Element Distribution

The mass medium equivalent diameters for major elements present in exhaust particles collected is presented by run number in Table 31. Cumulative mass distribution curves from which these values were extrapolated are shown in Appendix C.

4. HCl, NH_3, and H_2O

The level of HCl, NH_3, and H_2O present in exhaust particles as determined by mass spectrometry is shown in Table 32 by run number. Refer to analytical section for the significance and validity of comparing one run to another. Data is presented by major size fraction for each run.

5. Trace Metal Analysis

The trace metal content of collected exhaust particles as determined by emission spectrometry is presented in Table 33 by run number and sample source.

X-ray flourescence analysis of the small amount of particulate collected during run 56C (catalyst equipped vehicle) is shown in Table 34. Results are in ratios of amount present. Percentages could not be calculated reliably due to low sample weight.

TABLE 34

X-RAY FLUORESCENCE ANALYSIS
RUN 56C - SLIT SAMPLES A, B, C

	Values Expressed in Ratios		
Slit	A*	B	C
Pb	5.7	4.1	1.1
Ba	0.2	0.2	0.1
Br	0.14	0.1	0.06
Zn	0.5	3.6	1.4
Fe	1.1	4.6	0.5
Mn	0.2	0.1	-
Ca	0.14	0.1	0.1
K	0.08	0.5	0.06
Cl	1.0	0.4	0.4
S	3.3	2.4	1.1
P	2.3	1.3	0.8

*Results on Sample A are on the composite after removing magnetic portion

Sample letter also refers to sample location (see Figure 1)

TABLE 31

ENGINE STAND RUNS ONLY
ELEMENTAL MASS MEDIUM EQUIVALENT DIAMETER - Pb/Cl/Br/Organic

Run No.	Pb (MMED)	Cl (MMED)	Br (MMED)	Organics (MMED)
4	~0.10	<<0.10	<0.10	0.68
6	3.1	0.5	2.7	0.2
7	<<0.10	-	-	<<0.10
8	0.35	-	~0.10	0.3
9	2.0	1.2	-	<0.10
11	~0.10	~0.10	~0.10	<0.10
12	~0.10	~0.10	~0.10	<0.10
13	~0.10	~0.10	~0.10	<<0.10
14	<0.10	<0.10	<0.10	<<0.10
15		-	-	-
16	1.5	-	-	0.4
17	1.2	-	-	1.5
18	-	-	-	-
19	<0.10	>10.0	<0.10	~0.10
20	<0.10	<0.10	<0.10	0.42
21	-	-	-	<<0.10
22	1.35	1.90	<<0.10	<0.10
23	<0.10	<0.10	<0.10	<0.10
24	-	-	-	<0.10
25	-	-	-	<0.10
27	-	-	-	-
28	<0.10	6.0	<0.10	1.15
29	~0.10	3.3	<0.10	0.9
31	<0.10	<0.10	<0.10	<0.10
32	-	-	-	-
33	-	-	-	-
34	-	-	-	~0.10
37	-	-	-	-
38	-	-	-	-
40	-	-	-	0.31
41	-	-	-	-
42	-	-	-	-
43	-	-	-	-
44	-	-	-	<0.10
45	-	-	-	1.8
50	-	-	-	-
54	-	-	-	-

< = less than 0.10μ
<< = much less than 0.10μ
~ = approximately

TABLE 32

FRACTIONS OF HCl, NH_3, AND H_2O PRESENT IN EXHAUST PARTICLES

(Relative Units/mg Sample)
(Determination by Mass Spectrometry)

Run No.	Location	NH_3	H_2O	HCl	Sample Wt. (mg)
3	AP-5	0.018	0.059	0.002	1.15
3	6	.074	.097	.006	0.40
3	Filter	.148	.099	.113	8.70
4	AP-1	.013	.013	.004	28.20
4	2	.013	.014	.002	17.10
4	3	.017	.019	.002	11.25
4	4	.051	.048	.023	5.00
4	5	.143	.089	.134	4.90
4	6	.247	.089	.183	3.30
4	Filter	.258	.133	.161	4.90
4	S-1	.0017	.027	0	10.10
4	2	.003	.096	0	10.40
4	3	.03	.070	0	10.25
4	4	.03	.086	0	7.50
4	5	.03	.11	0	9.15
4	6	.03	.12	0	4.70
4	7	.03	.10	.002	2.00
5	AP-1	.337	.264	.081	0.50
5	2	.211	.188	.081	0.50
5	5	.010	.075	.004	0.80
5	S-1	.002	.28	0	9.45
5	2	.003	.27	.002	9.35
5	3	.002	.29	.001	10.57
5	3'	.004	.23	.008	1.20
5	4	.003	.28	.001	10.50
5	5	.002	.28	0	10.50
5	6	.002	.28	0	9.90
5	7	.002	.26	0	10.80
6	AP-1	.078	.027	.072	8.55
6	2	.025	.017	.012	6.70
6	3	.031	.033	.026	6.30
6	4	.052	.063	.037	3.25
6	5	.071	.114	.054	2.65
6	6	.086	.068	1.38	10.20
7	AP-1	.000	.026	.001	12.23
7	2	.001	.027	.000	15.85
7	3	.001	.030	.000	15.46
7	4	.002	.045	.001	8.66
7	5	.005	.081	.000	5.05
7	6	.012	.116	.003	2.61
7	Filter	.007	.125	.001	7.06
8	AP-3	.022	.020	.008	9.70
8	4	.042	.041	.012	6.40
8	5	.068	.072	.033	7.80
8	6	.049	.066	.016	9.50
8	Filter	.060	.046	.030	9.90
9	AP-1	.075	.043	.014	9.70
9	2	.031	.033	.002	10.30
9	3	.016	.034	.001	10.00
9	4	.022	.069	.002	7.75
9	5	.065	.164	.010	3.20
9	6	.093	.138	.006	1.60
9	Filter	.070	.080	.018	6.15
11	AP-1	.026	.016	.005	10.40
11	2	.011	.017	.003	8.90
11	3	.010	.026	.003	10.20
11	4	.010	.062	.003	5.80
11	5	.025	.152	.006	3.80
11	6	.036	.089	.007	4.40
11	Filter	.029	.046	.012	10.80

Code: AP- = Andersen collection plate-number (see Table 6 for size cutoff)
S- = Slit-number
SW- = Sweepings-letter

TABLE 32 (Cont.)

Run No.	Location	NH_3	H_2O	HCl	Sample Wt. (mg)
12	AP-1	0.006	0.019	0.007	10.61
12	2	.006	.017	.008	10.36
12	3	.003	.019	.005	9.84
12	4	.017	.041	.005	6.45
12	5	.051	.057	.024	6.74
12	6	.068	.050	.045	7.90
12	Filter	.072	.039	.036	6.41
13	AP-1	.027	.021	.005	10.70
13	2	.009	.020	.002	11.30
13	3	.007	.031	.002	9.00
13	4	.008	.067	.002	5.10
13	5	.022	.127	.008	3.55
13	6	.033	.074	.005	3.55
13	Filter	.030	.037	.009	9.10
14	AP-1	.028	.023	.006	7.40
14	2	.008	.012	.001	9.61
14	3	.006	.017	.001	7.66
14	4	.008	.034	0	3.62
14	5	.043	.067	.009	3.30
14	6	.084	.062	.007	1.90
14	Filter	.092	.042	.048	6.21
16	AP-1	.157	.318	.012	1.17
16	2	.019	.255	.007	1.17
16	3	.012	.216	.004	0.87
16	4	.005	.142	.007	0.50
16	5	.008	.273	.005	0.65
16	6	.003	.188	.006	0.55
16	Filter	.007	.231	.000	0.30
17	AP-1	.172	.333	.013	1.05
17	2	.031	.588	.016	0.30
17	3	.008	.180	.006	0.70
17	4	.006	.206	.005	0.65
17	5	.004	.244	.007	0.55
17	6	.004	.294	.008	0.40
17	Filter	.002	.066	.003	1.20
18	AP-1	.052	.050	.051	12.30
18	2	.027	.054	.009	7.74
18	3	.012	.090	.032	9.83
18	4	.009	.146	.029	9.42
18	5	.009	.110	.037	11.13
18	6	.011	.068	.021	9.24
18	Filter	>.003	>.054	>.009	13.81
18	S-1	.001	.15	.004	11.31
19	AP-1	.027	.027	.006	14.2
19	2	.008	.017	.002	19.16
19	3	.005	.019	.002	16.15
19	4	.011	.039	.003	6.48
19	5	.036	.075	.015	4.68
19	6	.073	.067	.030	4.40
19	7	.071	.047	.022	7.95
19	Filter	>.122	>.050	>.05	4.60
19	S-1	~ 0	.14	~ 0	8.07
20	AP-1	.030	.022	.008	17.16
20	2	.011	.014	.001	17.12
20	3	.008	.018	.001	12.02
20	4	.0183	.0315	.0013	6.56
20	5	.054	.058	.007	5.74
20	6	.123	.064	.065	3.58
20	7	.096	.056	.078	8.85
20	Filter	>.055	>.063	~ 0	0.81
20	S-1	.019	.068	.005	11.73
20	S-7	.070	.072	.014	8.95

TABLE 32 (Cont.)

Run No.	Location	NH_3	H_2O	HCl	Sample Wt. (mg)
21	AP-1	0.22	0.14	0.038	3.04
21	2	.074	.086	.0028	2.31
21	3	.038	.095	.0011	1.57
21	4	.027	.15	.0018	1.10
21	5	.032	.21	.0018	0.71
21	6	.059	.24	~ 0	0.37
21	S-1	~ 0	.44	.014	10.85
21	2	~ 0	.59	.014	9.61
21	3	~ 0	.56	~ 0	3.08
21	4	.002	1.10	~ 0	0.26
22	AP-1	.005	0.300	.018	0.705
22	2	.002	.293	.021	0.40
22	3	.006	.250	.008	0.85
22	4	.012	.330	.010	0.70
22	5	.009	.465	.006	1.20
22	6	.008	.664	.015	0.40
22	Filter	> .001	> .109	> .002	3.05
22	S-1	~ 0	.45	.002	10.31
22	2	~ 0	.53	~ 0	10.20
22	3	~ 0	.64	.42	11.73
22	4	~ 0	.67	.001	2.33
23	AP-1	1.024	.003	~ 0	8.3
23	2	0.009	.019	~ 0	9.9
23	3	.012	.032	~ 0	7.05
23	4	.029	.150	.002	3.00
23	5	.077	.377	.010	2.40
23	6	.189	.248	.029	1.70
23	7	.179	.157	.071	3.90
23	Filter	> .154	> .077	> .133	8.30
23	S-1	~ 0	.33	~ 0	9.21
23	2	~ 0	.28	~ 0	11.08
23	3	~ 0	.36	~ 0	10.76
23	4	~ 0	.36	~ 0	3.19
23	5	.002	.82	~ 0	0.94
24	AP-1	.015	.017	.0013	5.12
24	2	.0087	.014	~ 0	4.94
24	3	.013	.025	~ 0	3.80
24	4	.037	.160	~ 0	0.66
24	5	.160	.23	~ 0	0.55
24	6	.23	1.49	~ 0	0.31
24	7	.47	0.27	.021	1.18
24	Filter	>.037	>.052	>.034	8.66
25	AP-1	.032	.028	.002	4.53
25	2	.0094	.031	~ 0	5.93
25	3	.012	.078	~ 0	3.74
25	4	.046	.084	~ 0	1.18
25	5	.095	.26	.071	0.66
25	6	.11	.35	~ 0	0.70
25	7	.40	.28	.30	1.17
25	Filter	>.027	>.048	>.055	9.38
28	AP-1	.039	.027	.0008	5.80
28	2	.01	.02	.0008	6.66
28	3	.01	.023	.0008	6.40
28	4	.024	.094	.003	2.19
28	5	.078	.087	.0006	1.26
28	6	.100	.330	~ 0	0.31
28	Filter	>.025	.027	.004	7.42
29	AP-1	.006	.20	~ 0	0.18
29	2	.011	.19	~ 0	0.21
29	3	.005	.32	~ 0	0.36
29	4	.008	.22	~ 0	0.38
29	5	.018	.22	~ 0	0.16
29	6	.340	.87	~ 0	0.14
29	Filter	>.002	>.026	~ 0	7.31
29	Total Hot	~ 0	-	~.001	11.05

TABLE 32 (Cont.)

Run No.	Location	NH_3	H_2O	HCl	Sample Wt. (mg)
31	AP-1	0.019	0.019	0.002	8.44
31	2	.026	.022	.003	4.60
31	3	.038	.031	.004	3.32
31	4	.041	.12	.0002	1.30
31	5	.12	.11	.007	1.09
31	6	.10	.24	0	0.4
31	Filter	>.134	>.048	>.47	12.53
31	4 cfm	>.14	>.003	>.13	9.04
33	Filter	~ 0	.053	.001	9.17
33	Filter	.019	.046	.002	9.0
34	AP-1	.375	.260	.073	0.93
34	2	.177	.585	.029	2.68
34	3	.043	.113	.010	2.55
34	4	.039	.163	.010	2.08
34	5	.055	.128	.010	2.89
34	6	.075	.215	.010	0.98
34	7	.048	.058	.011	4.03
34	Filter	.009	.038	.002	9.46
36	Filter CS	.003	.048	.002	8.69
36	Filter SS	.001	.021	~ 0	9.53
38	S-1	~ 0	.076	.001	15.0
38	3	.087	.121	.041	12.75
38	5	.328	.169	.507	7.02
38	7	.507	.402	.153	1.31
38	Filter	.557	.174	.235	2.18
40	AP-1	.028	.120	~ 0	0.77
40	2	.024	.087	~ 0	2.03
40	3	.016	.142	~ 0	2.28
40	4	.016	.146	~ 0	1.5
40	5	.029	.163	~ 0	1.66
40	6	.091	.370	~ 0	0.24
40	Filter	.07	.057	.007	8.38
41	S-1	.005	.214	~ 0	1.77
41	3	.001	.299	~ 0	6.47
41	5	.001	.331	~ 0	2.01
41	Filter	.002	.303	~ 0	9.9
42	S-1	~ 0	.077	~ 0	3.42
42	5	~ 0	.437	~ 0	2.32
42	7	~ 0	.5217	~ 0	0.35
42	Filter	~ 0	.13	~ 0	11.0
43	SW-A	.366	~ 0	~ 0	4.8
43	E	.447	.004	~ 0	3.1
43	F	.002	.029	0	9.98
43	G	.464	.004	~ 0	0.74
44	AP-1	.015	.978	~ 0	0.21
44	2	.013	.567	0	0.23
44	3	.031	.847	0	0.37
44	4	.030	1.000	0	0.36
44	5	.027	0.838	0	0.54
44	6	.115	1.055	0	0.33
44	7	.036	0.328	0	0.40
44	Filter	~ 0	.328	0	7.4

TABLE 32 (Cont.)

Run No.	Location	NH_3	H_2O	HCl	Sample Wt. (mg)
45	AP-1	0.063	0.319	~ 0	0.15
45	2	.213	2.246	~ 0	0.04
45	3	~ 0	2.30	~ 0	0.03
45	4	~ 0	0.862	~ 0	0.07
45	5	.085	1.83	~ 0	0.05
45	6	.018	0.329	~ 0	0.21
45	7	.103	.525	~ 0	0.21
45	Filter	.037	.048	0.014	11.02
46	AP-1	.024	.596	~ 0	0.26
46	2	.026	.673	~ 0	0.18
46	4	.012	.939	~ 0	0.16
46	5	.003	.538	~ 0	0.26
46	6	~ 0	.543	~ 0	0.18
48	AP-1	.019	.6	~ 0	0.20
48	2	.004	.655	~ 0	0.20
48	3	.010	1.091	~ 0	0.10
48	4	.0009	0.795	~ 0	0.11
48	5	.015	.495	~ 0	0.19
48	6	~ 0	1.67	~ 0	0.12
53	AP-1	.003	0.42	~ 0	0.20
53	2	.069	1.41	~ 0	0.10
53	3	.17	0.79	~ 0	0.10
53	4	.004	.48	~ 0	0.15
53	5	.006	.30	~ 0	0.20
53	6	.014	4.82	~ 0	0.20
56B*	SW-J	.008	.60	~ 0	6.25
56B*	H	.20	.55	.18	9.51
56C**	G	.004	.56	~ 0	10.26
56C**	I	.007	.65	~ 0	5.28
56C**	K	.008	.76	~ 0	5.35
56B*	AP-1	.42	1.2	~ 0	0.18
56B*	2	-	-	-	0.01
56B*	3	.018	0.69	~ 0	0.10
56B*	4	.005	.30	~ 0	0.25
56B*	5	.010	.52	~ 0	0.30
56B*	6	-	-	-	0.01
56C**	AP-1	.032	.99	~ 0	1.23
56C**	2	.026	1.60	~ 0	0.53
56C**	3	.023	1.30	~ 0	0.93
56C**	4	.026	1.60	~ 0	0.53
56C**	5	.029	2.30	~ 0	0.92
56C**	6	.048	2.90	~ 0	0.24

*Steady-state 30 mph; both sides of engine used.
**Steady-state 60 mph; both sides of engine used.

Code: AP- = Andersen Plate-number
S- = Slit-number
SW- = Sweepings-letter

TABLE 33

EXHAUST PARTICULATE - TRACE METALS

(Expressed as Weight Percent)

Run No.	Fe	Ni	Cu	Al	Ca	Si	Mg	Mn	Cr	Sn	Zn	Ti	Mo	Co	Cd	C	Sample Source*
11	0.16	<0.01	0.018	0.032	0.13	0.039	0.066	<0.005	<0.01	<0.01	0.068	<0.01	-	-	-	-	AP-1
	.19	<.01	.026	.08	.10	.038	.063	<.005	.012	<.01	.059	<.01	-	-	-	-	2
	.15	<.025	.034	.048	.18	.036	.11	<.01	<.025	<.025	.09	<.025	-	-	-	-	3
	.24	<.025	.040	.11	.30	.068	.32	<.01	<.025	<.025	.14	<.025	-	-	-	-	4
	.18	<.025	.034	.11	.36	.050	.43	<.01	<.025	<.025	.14	<.025	-	-	-	-	5
	.15	<.025	.054	.12	.23	.038	.16	<.01	<.025	<.025	.11	<.025	-	-	-	-	6
	.098	<.01	.008	.023	.095	<.01	.005	<.005	<.01	<.01	.09	<.01	-	-	-	-	Filter
12	3.5	.017	.010	.080	.031	.046	.71	.074	.075	.019	4.4	<.010	0.010	-	-	-	S-1
	4.3	.012	.011	.062	.063	.060	.15	.060	.059	.017	9.3	<.010	.007	-	-	-	S-2
	3.0	.011	.010	.055	.025	.039	.33	.036	.054	.010	5.4	<.010	.007	-	-	-	SW-A
	4.9	.014	.011	.075	.032	.087	.57	.067	.085	.015	7.0	<.010	.008	-	-	-	B
	3.1	.011	.019	.076	.036	.095	.48	.036	.056	.012	9.7	<.010	.005	-	-	-	C
	2.5	.02[illegible]	.016	.13	.088	.084	.65	.10	.13	.016	4.2	<.010	.008	-	-	-	D
	1.6	<.010	.009	.063	.078	.13	.46	.015	.043	<.01	0.51	<.010	.006	-	-	-	E
	0.95	<.010	.008	.064	.050	.054	.33	.011	.030	<.01	.32	<.010	.004	-	-	-	F
	1.3	<.010	.010	.043	.12	.079	.38	.012	.034	<.01	.41	<.010	.005	-	-	-	G
	0.16	<.01	.038	.074	.17	.061	.086	<.005	<.01	<.01	.069	<.01	-	-	-	-	AP-1
	.14	<.01	.025	.027	.17	.03	.083	<.005	<.01	<.01	.051	<.01	-	-	-	-	2
	.31	<.01	.032	.044	.15	.034	.073	<.005	<.01	<.01	.061	<.01	-	-	-	-	3
	.39	<.025	.027	.043	.29	<.025	.14	<.01	<.025	<.025	.11	<.025	-	-	-	-	4
	.19	<.025	.027	.072	.27	.072	.22	<.01	<.025	.027	.11	.70	-	-	-	-	5
	.16	<.025	.028	.11	.29	.046	.20	<.01	<.025	<.025	.088	<.025	-	-	-	-	6
	.18	<.01	.006	.010	.058	<.01	.027	<.005	<.01	<.01	.069	<.01	-	-	-	-	Filter
29	2.1	<.4	.4	.6	2.3	.5	1.8	<.2	<.4	<.4	<.8	<.4	-	-	-	-	AP-1
	3.4	1.0	.4	1.0	1.8	1.8	1.8	.3	<.4	<.4	.8	<.4	-	-	-	-	2
	2.4	0.6	.4	1.1	2.0	2.7	1.6	.2	<.4	<.4	.8	<.4	-	-	-	-	3
	3.5	.7	.3	1.0	1.8	1.2	1.5	.2	<.4	1.4	1.2	<.4	-	-	-	-	4
	4.7	.6	.4	1.0	1.5	1.6	1.2	.2	<.4	0.4	1.1	<.4	-	-	-	-	5
	4.3	1.9	.3	3.7	4.1	11.7	5.0	.8	<.6	<.6	<1.0	<.6	-	-	-	-	6
	2.5	0.3	.1	35.5	44.5	2.6	11.7	.1	<.2	<.2	2.9	.8	-	-	-	-	Filter**
31	0.1	.09	.04	0.1	0.2	0.08	0.2	.03	<.05	<.05	0.1	<.05	-	-	-	-	AP-1
	.1	.07	.05	.1	.3	.4	.2	.02	<.05	<.05	.2	<.05	-	-	-	-	2
	.09	<.05	.06	.4	.4	.3	.2	.01	<.05	<.05	.2	<.05	-	-	-	-	3
	<.05	<.05	.02	.2	.3	.08	.1	.02	<.05	<.05	<.1	<.05	-	-	-	-	4
	<.05	<.05	.01	.1	.1	.07	.1	.02	<.05	<.05	<.1	<.05	-	-	-	-	5
	<.05	<.05	.02	.2	.3	.09	.1	.01	<.05	<.05	<.1	<.05	-	-	-	-	6
	.04	<.03	<.01	.1	.2	.1	.1	.01	<.03	<.03	<.05	<.03	-	-	-	-	Filter
34	.18	<.01	.005	.097	.48	.10	.087	<.005	<.01	<.01	.088	<.01	-	-	-	-	Filter
38	23.0	.036	.053	.094	1.3	.1	.16	.074	.022	<.01	.28	.01	<.005	0.035	<0.005	-	SW-F
	27.0	<.02	.024	.044	0.51	.07	.078	.062	.020	<.02	.16	.02	<.01	<.01	<.01	-	H
	1.3	<.05	.055	.500	2.6	.08	.25	<.01	<.05	<.05	.12	.05	<.025	<.025	<.025	-	J

*Code: AP- = Andersen Plate-number S- = Slit-number SW- = Sweepings-letter

**Values could be suspect due to sample size and impurities of the blank.

TABLE 33 (Cont.)

Run No.	Fe	Ni	Cu	Al	Ca	Si	Mg	Mn	Cr	Sn	Zn	Ti	Mo	Co	Cl	C	Sample Source*
40	0.38	<0.05	0.05	1.3	2.9	4.3	0.94	<0.01	0.05	<0.05	<0.01	<0.05	-	-	-	-	Filter
	5.0	<.02	.052	0.046	<0.02	0.20	.66	.016	<.02	<.02	.92	.02	<0.01	<0.01	<0.01	-	SW-H
	4.4	<.02	.058	.044	.028	.10	1.0	.014	<.02	<.02	.66	<.02	<.01	<.01	<.01	-	J
	2.5	<.05	.24	.22	.17	.05	0.60	<.01	<.05	<.05	.95	<.05	<.025	<.025	<.025	-	L
	0.22	<.05	.06	.14	.30	.2	.30	<.01	<.05	<.05	.80	<.05	-	-	-	-	AP-1 thru 6
	.10	<.05	.04	<.05	.15	.1	.22	<.01	<.05	<.05	.52	<.05	-	-	-	-	AP-1 thru 6
41	.15	<.01	.009	.21	.57	.2	.19	<.005	.016	<.01	.062	<.01	-	-	-	-	Filter
42	7.1	<.05	4.8	.58	5.2	.3	.27	.070	<.05	<.05	1.1	<.05	<.025	<.025	<.025	-	S-2
	21.0	<.10	0.43	2.2	7.9	.3	<.10	.050	<.1	<.1	2.8	<.10	<.06	<.06	<.06	-	4
	4.1	<.50	.04	1.7	3.0	.5	<.50	<.1	<.5	<.5	2.7	<.5	<.25	<.25	<.25	-	6
	19.0	<.02	.11	2.2	1.8	.4	.20	.14	.023	<.02	0.60	<.02	<.01	<.01	<.01	-	SW-I
	51.0	.032	.44	1.0	2.3	.2	.16	.19	<.02	<.02	.76	<.02	<.01	<.01	<.01	-	K
	2.1	<.05	.28	0.39	0.51	.3	.095	<.01	<.05	<.05	2.0	<.05	<.025	<.025	<.025	-	M
	1.0	<.05	.18	4.5	13.6	3.6	3.8	<.01	.23	<.05	0.86	<.05	-	-	-	-	Filter
43	53.0	.024	.048	0.10	0.12	0.06	0.23	.13	.019	<.01	.59	<.01	.007	<.005	.010	-	SW-G
	44.0	.095	.67	.27	.39	.2	.60	.17	<.05	<.05	.84	<.05	<.025	<.025	<.025	-	I
	-	.3	-	1.0	1.0	.8	.50	<.2	<.20	<.2	.80	<.02	<.13	<.13	<.13	-	K
44	1.0	<.02	.044	0.070	0.072	.08	2.2	.008	<.02	<.02	1.7	<.02	<.01	<.01	<.01	-	SW-H
	11.0	<.02	.038	.090	.084	.20	2.5	.018	<.02	<.02	1.7	<.02	<.01	<.01	<.01	-	J
	1.8	<.05	5.2	.35	.60	.30	1.8	<.01	<.05	<.05	1.9	<.05	<.025	<.025	<.025	-	L
	0.07	<.05	0.02	<.05	.29	.1	0.11	<.01	<.05	<.05	<0.10	<.05	-	-	-	-	Filter
	0.46	<.05	.03	.12	.38	<.1	.61	<.01	<.05	<.05	1.2	<.05	-	-	-	-	AP-1 thru 6
45	33.0	<.02	.13	.32	.19	.3	3.2	.11	<.02	<.02	1.9	<.02	<.01	<.01	.008	-	SW-F
	23.0	<.05	.82	.33	.24	.3	0.14	.050	<.05	<.05	2.9	<.05	<.025	<.025	<.025	-	H
	36.0	<.5	2.1	3.0	1.5	<.5	3.0	<.1	<.5	<.5	3.0	<.5	<.25	<.25	<.25	-	J
46	43.0	.036	0.060	0.12	0.12	.1	0.10	.14	<.01	<.01	10.0	<.01	<.006	<.005	.011	-	SW-G
	51.0	.035	.21	.19	.09	.06	.11	.15	<.01	<.01	10.0	<.01	<.006	<.005	.009	-	I
	28.0	<.1	14.0	.40	2.6	.5	.60	<.03	<.01	<.01	3.6	<.01	<.06	<.06	<.06	-	K
48	42.0	.030	0.49	.30	0.44	.1	.22	.13	<.02	<.02	2.1	<.02	<.01	<.01	<.01	-	SW-F
	29.0	.011	.056	.26	.22	.1	.16	.092	<.01	<.01	1.2	<.01	.006	<.001	.004	-	H
	58.0	.040	.094	.44	.46	.2	.26	.18	<.02	<.02	2.2	<.02	<.01	<.01	.014	-	J
53	13.0	.013	.33	.12	.72	.04	.14	.030	<.01	<.01	2.4	<.01	<.005	<.005	<.005	-	SW-I
	29.0	.022	.080	1.1	8.50	.70	1.5	.100	.020	<.02	4.5	<.02	<.01	<.01	.009	-	G
	0.90	<.05	.090	0.32	2.2	<.10	0.27	<.01	<.05	<.05	<0.1	<.05	<.025	<.025	.025	-	Filter
56	4.5	.008	.03	.10	0.09	-	5.1	.06	<.05	<.05	4.7	<.003	-	-	-	31.65	SW-I
	3.6	.004	.03	.10	.10	-	5.2	.04	<.05	<.05	3.6	<.003	-	-	-	38.69	K
	5.6	.07	.30	1.8	.08	-	3.9	.20	.5	<.05	3.0	<.003	-	-	-	18.19?	F
	4.5	.01	.10	1.0	.10	-	5.1	.10	.2	<.05	4.8	<.003	-	-	-	34.47	H
	2.6	.006	.06	0.20	.10	-	4.0	.04	<.05	<.05	3.6	<.003	-	-	-	37.92	J
	2.6	.004	.08	.20	.10	-	4.3	.06	.07	<.05	3.0	<.003	-	-	-	37.00	L
	0.34	.1	.09	.13	.78	-	.12	<.02	.68	.1	<0.01	<.1	-	-	-	-	Filter

*Code: AP- = Andersen Plate-number S- = Slit-number SW- = Sweepings-letter

6. Crystalline Species

X-ray diffraction analysis was made of selected exhaust particle samples. The crystalline species present in shown by run number in Table 35.

TABLE 35
X-RAY DIFFRACTION ANALYSIS OF EXHAUST PARTICLES

Run No.	Source	Crystalline Species Present
8	Andersen	Pb Br_2
	Plate 6	UP 1875* chief constituent on AP**-6
	Filter	and filter
9	Andersen	Pb Cl_2
	Plate #6	UP 1875 (high Cl) and 5-10% PbCl_2 on AP-6
	Filter	UP 1875 only, filter
11	Andersen	Pb (Cl, [illegible])$_2$
	Plate #6	UP 1875 present (20-30%) on AP-6 and filter
	Filter	
12	Andersen	Pb (Cl, Br)_2
	Plate #1	UP 1875 5-10% on AP-1, 10-20% on filter
13	Andersen	Pb (Cl, Br)_2
	Plate #6	UP 1875 10-20% on AP-6 and 20-30% on filter
	Filter	
14	Andersen	Pb (Cl, Br)_2
	Plate #6	UP 1875 50% on AP-6 and 30-40% on filter
	Filter	

*UP 1875 = Unidentified Pb-Cl-Br structure

**AP = Andersen Plate

Table 35 (Contd.)

Run No.	Source	Crystalline Species Present
15	Andersen Plates #1, #4, and #6	Quartz; Calcite; NaCl; NH_4Cl - all weak lines
16	Andersen Plates #1, #3, and #6	$Pb\ (Cl, Br)_2$; NH_4Cl; $Pb_5\ OH\ (PO_4)_3$
17	Andersen Plates #1, #3, and #6	$Pb\ (Cl, Br)_2$; NH_4Cl; $Pb_5\ OH\ (PO_4)_3$; $4Pb \cdot Pb\ SO_4$ (trace)
42	Dilution tube Slit samples Fe	NaCl major component Fe_3O_4 10-20 Fe_2O_3 10-20 α FeOOH 10-20 Quartz <5
	Dilution tube Sweepings	NaCl major component Fe_3O_4 5-10 Fe_2O_3 5-10 Quartz <5
45	Dilution tube Sweepings	$Pb\ (Cl, Br)_2$ - Cl:Br 1:1, major componer Fe_3O_4 20-30 Fe_2O_3 10-20 Fe ~5
46	Dilution tube Slit samples	Fe_3O_4 40-60 Fe_2O_3 30-40 ZnO 10-20 Fe ~5
	Dilution tube Sweepings	Fe_3O_4 40-60 Fe_2O_3 20-30 ZnO 20-30 Fe ~5

7. Particle Morpheus

Particle morpheus has been examined by optical microscopy, transmission electron and scanning electron microscopy. Optical techniques have been used to evaluate particle birefringence, and general size and shape. Another study conducted by this laboratory for the Environmental Protection Agency(11), Office of Air Programs was directed toward the examination of the fate of exhaust particles in the exhaust system itself. That study found the birefringent techniques showed a decrease in discrete particle crystalline character as the particles approached the tailpipe. Not surprisingly, in a similar examination of the exhaust particles collected after emission from the tailpipe in this study the birefringence was found to be very low, indicating that most particles are broken up, conglomerates, with very few single, discrete particle species. Examples are shown in Figures 29 through 32.

The transmission electron microscope (TEM) was employed in this study to examine the very fine particles being emitted from the engine. Representative examples are shown in Figures 33 through 36. During examination of exhaust particulate with the TEM, particle size was observed to decrease markedly. Further investigation showed that this was caused by the vaporization of condensed organics on particles (which apparently act as a condensation nucleation site during air dilution and cooling of the exhaust) due to the high intensity electron beam.

The scanning electron microscopy (SEM) in combination with an X-ray fluorescence detector had been used to examine individual exhaust particles. Typical exhaust particles are shown in Figures 37-42. The capability in separating elemental components in exhaust particles is shown in Figures 43-70. Specific analysis of selected runs are discussed in detail.

Run No. 21

Particle documentation on Plate 1 of the Andersen sampler is found on Figure 43 and Figure 45. Figure 44B is typical of the fines on Plate 1. Spectrum Figure 46 recording Pb:Br:Cl is typical of particle type Figure 43 C and D. The log-type crystals (Figure 44 B and C) have less chlorine than those of Figure 43 C and D. This log-type crystal is more easily found near impingement areas indicating higher density.

In an extensive search of Plate 1, no particles were found which did not contain lead. Likewise, some of the particles with spectra of Pb:Cl:Br were non-crystalline (Figure 44 D). Iron was present in many particles but no correlation between the presence of iron and the morphology of the particle could be made.

X-ray analysis data was collected at impingement points. Each area examined, Plates 1, 4, 7, and the final filter (Figures 47, 48, 49, 50, respectively), revealed the presence of Pb:Br:Cl. The ratio of chlorine to bromine decreases from Plate 1 to 7 with a similar ratio on the final filter as was found on Plate 1. Small amounts of iron are found on Plates 1 and 7 with copper and zinc being on the final filter. Figure 51 is a spectrum of an unused or blank filter paper.

Run No. 24

X-ray data was collected at impingement points on Plate 1 (Figure 52) and Plate 4 (Figure 53). The spectrum includes Pb:Br:Cl and Si with the chlorine to bromine ratio being decreased on Plate 4. The base line on the spectra suggests the presence of organics.

Run No. 25

X-ray analysis is recorded on Plates 1, 4, 7 and Filters 1, 2 and 3 (Figures 54, 55, 56, 57, 58, 59, respectively). The elements present in all of these positions are Pb:Br:Cl and

Si with the only difference being in the ratio of one element to another. The additional elements of K, Ca, Ba, and Zn found in the filter samples is due principally to the filter and not the particulates. The base line on the spectra from Plates 1 and 7 indicate the presence of high organics.

Run No. 39

X-ray analysis is recorded from impingement points on Plates 3 and 6 (Figures 60 and 61). The major component is iron with minor amounts of Cl, Ca, Cr, and Cu. Peaks are also recorded at 1.48 Kev, which could be bromine or aluminum or a combination of both, and at 2.31 which could be the lead M energy line or the Kα energy line of sulfur. Lead is definitely present due to the Lα energy band, but sulfur may also be present.

Run No. 41

X-ray spectra from impingement points on Plates 4 and 7 (Figures 62 and 63) show high amounts of sulfur to be present. Other elements in lesser amounts include Al, Si, K, Ca, Cr, Mn, Cu, Zn, and Pb. More iron and silicon is found on Plate 7 than on Plate 4.

Run No. 42

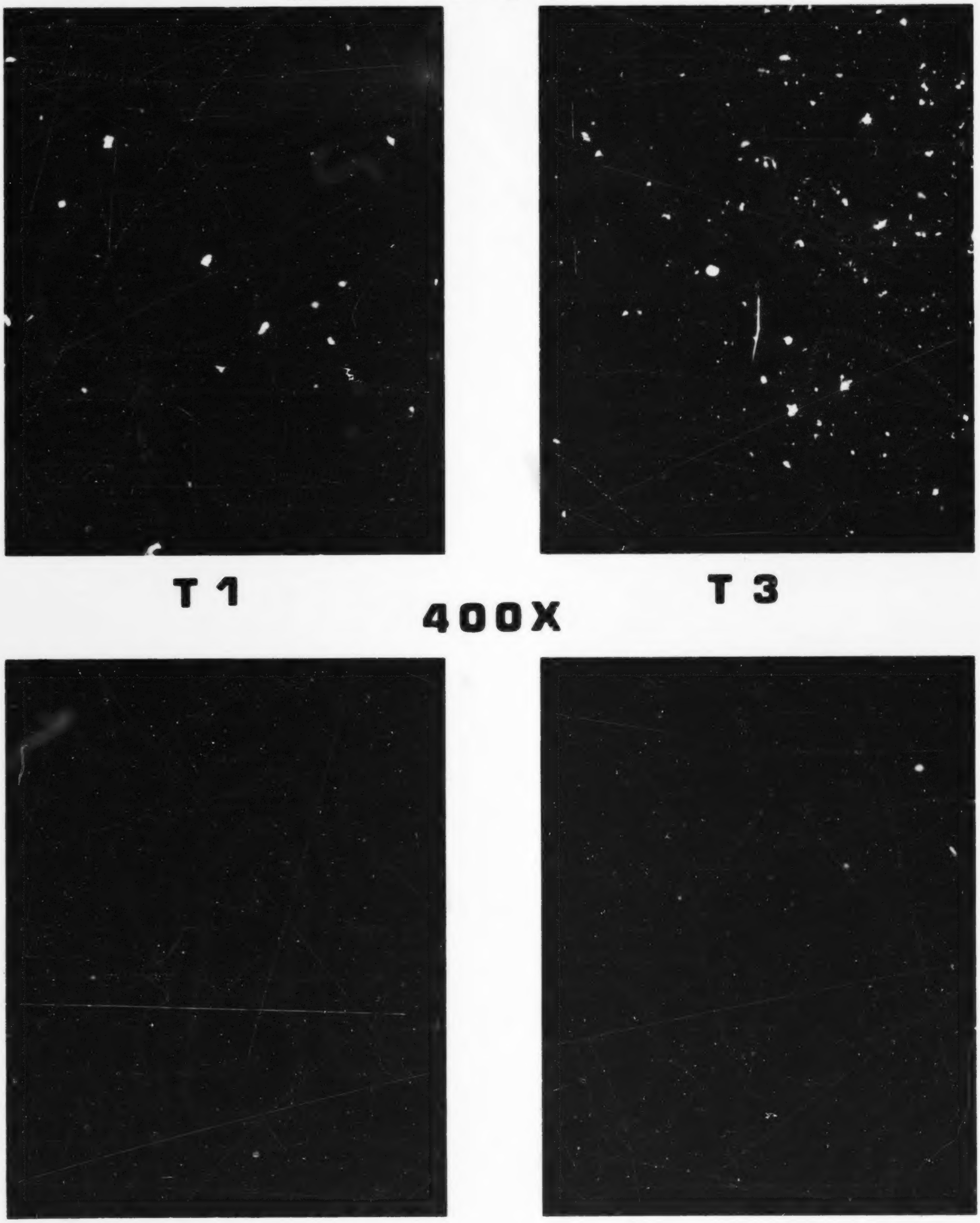
Very little particulate was collected from this run. X-ray analysis was made on Plates 1, 4, and 7 (Figures 64, 65, 66) with several impingement points being scraped together to have enough particulate for a good analysis. Elements found on each of these plates include Si, P, Pb, S, Cl, Ca, Cr, Mn, Fe, Cu, Zn, Br, and possibly Al. Plate 7 also includes Ag and K. The silver may be due to the conductive paint used to attach the substrate to the specimen stub.

Individual particle analysis from Plate 1 indicates various species of particulate with Pb:Br:Cl being the most frequent. These Pb:Br:Cl particles had the crystalline shape of the typical particles, Figure 45 A or B. Particles and X-ray analysis of the individual particles are shown in Figures 45, 67, 68, 69, and 70.

The individual particles from Plates 4 and 7 are very small and not well defined; therefore, no individual particle analysis was made on these plates.

(Text continues on page 165)

Figure 29. Exhaust Particulate on Andersen Plates by OM - From Run #9



T 1

T 3

400X

T 6

M

Figure 30. Exhaust Particulate on Andersen Plates by OM - From Run #8

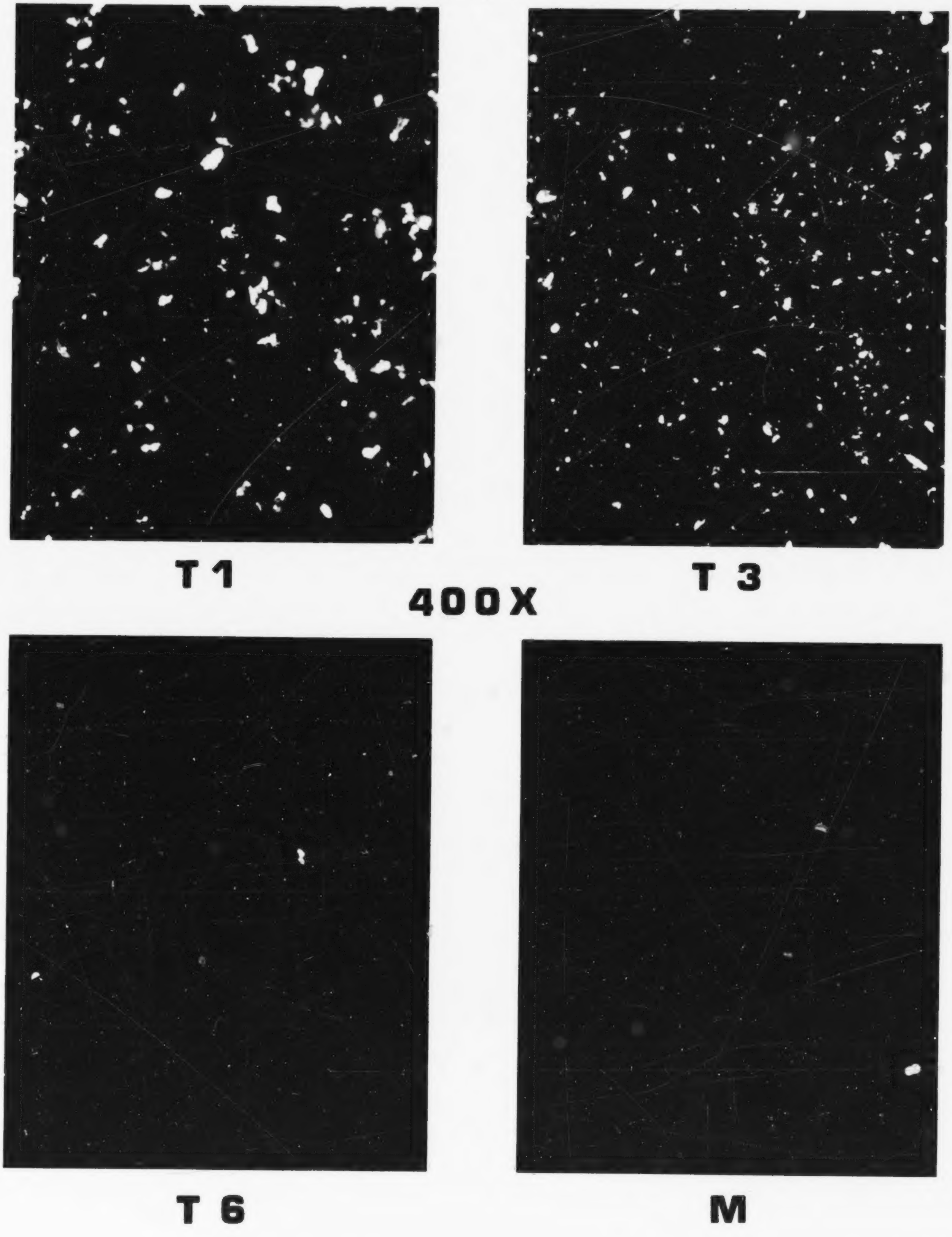
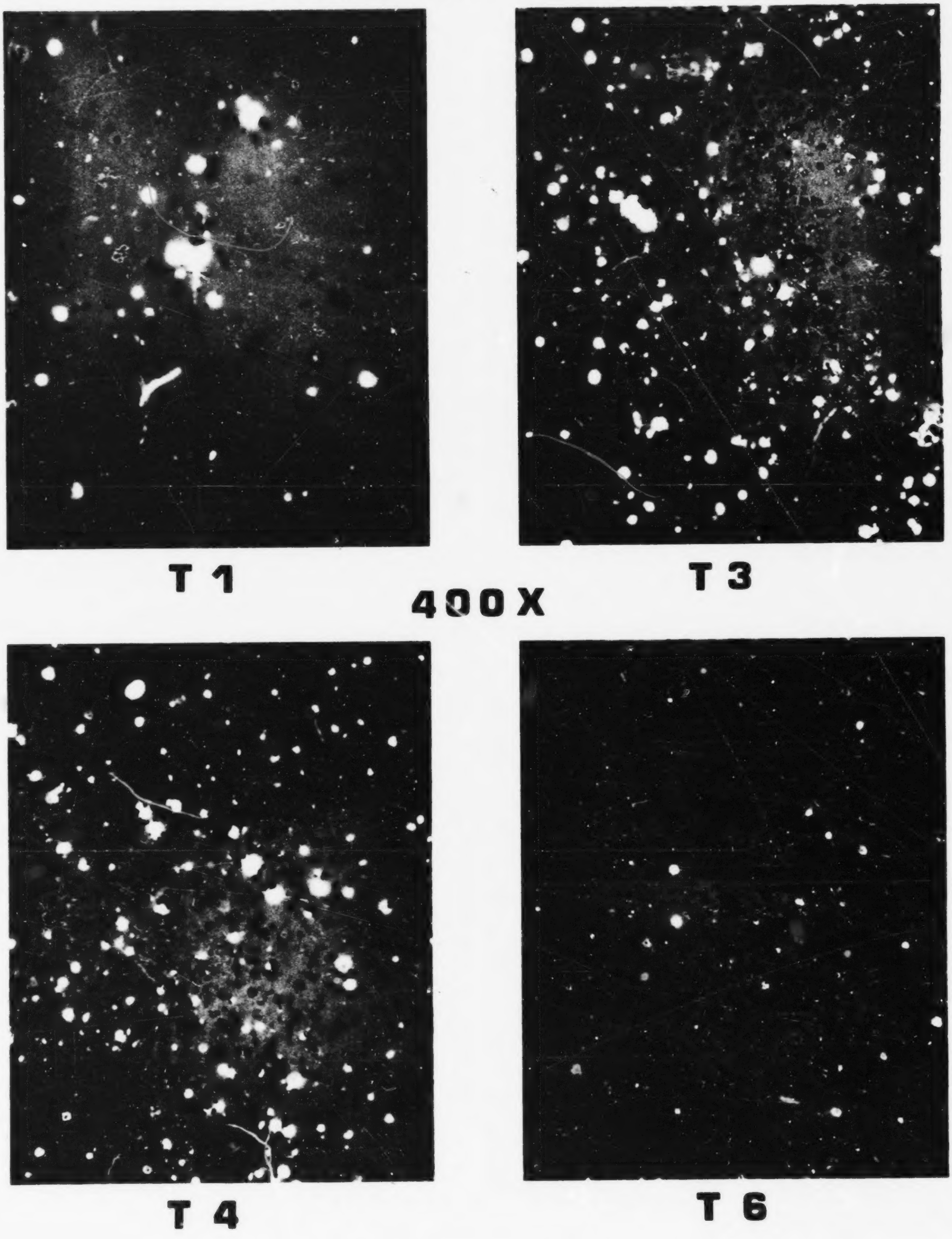

T 1
T 3
400X
T 6
M

Figure 31. Exhaust Particulate on Andersen Plates by OM - From Run #15



T 1

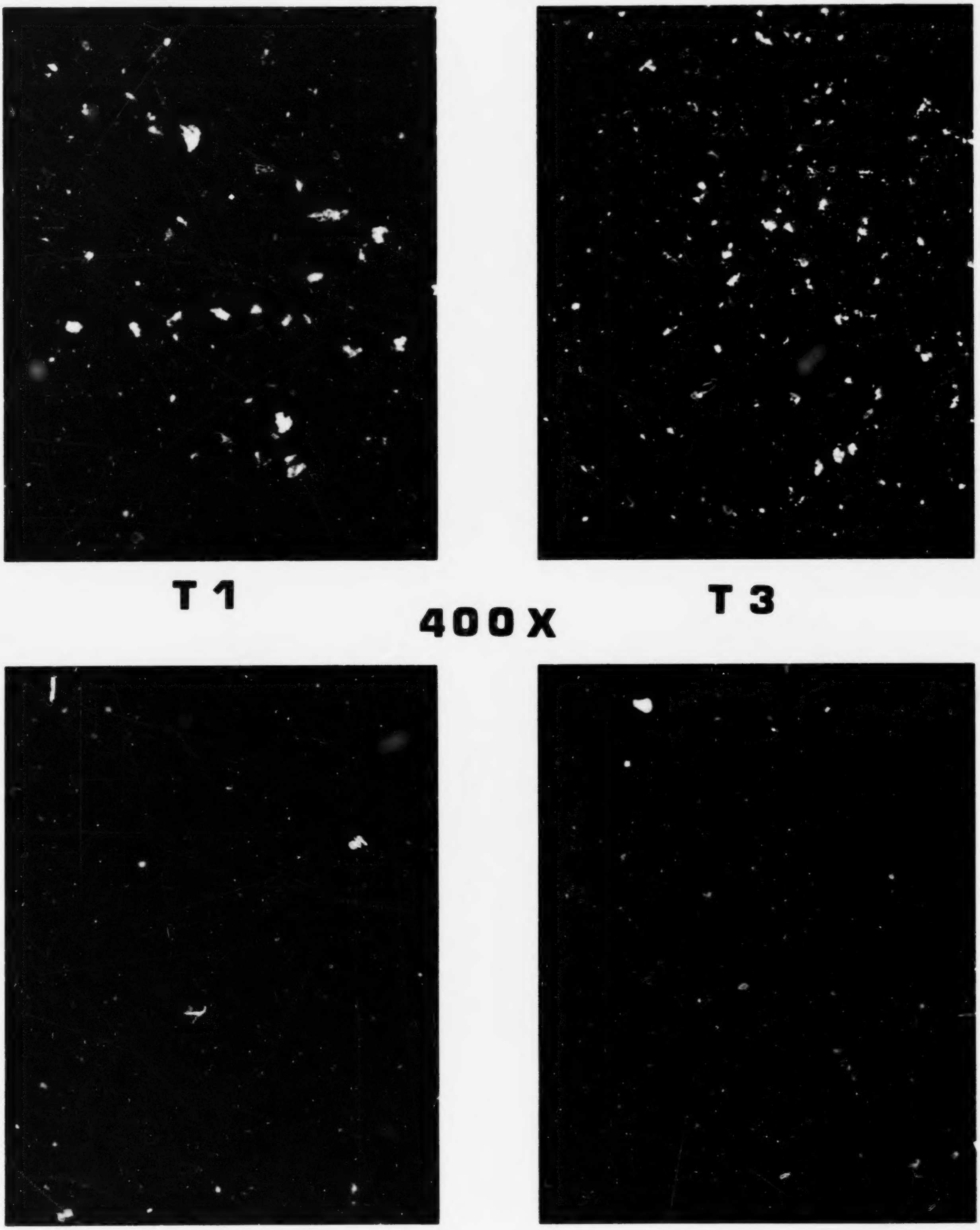
T 3

400X

T 4

T 6

Figure 32. Exhaust Particulate on Andersen Plates by OM - From Run #11



T 1

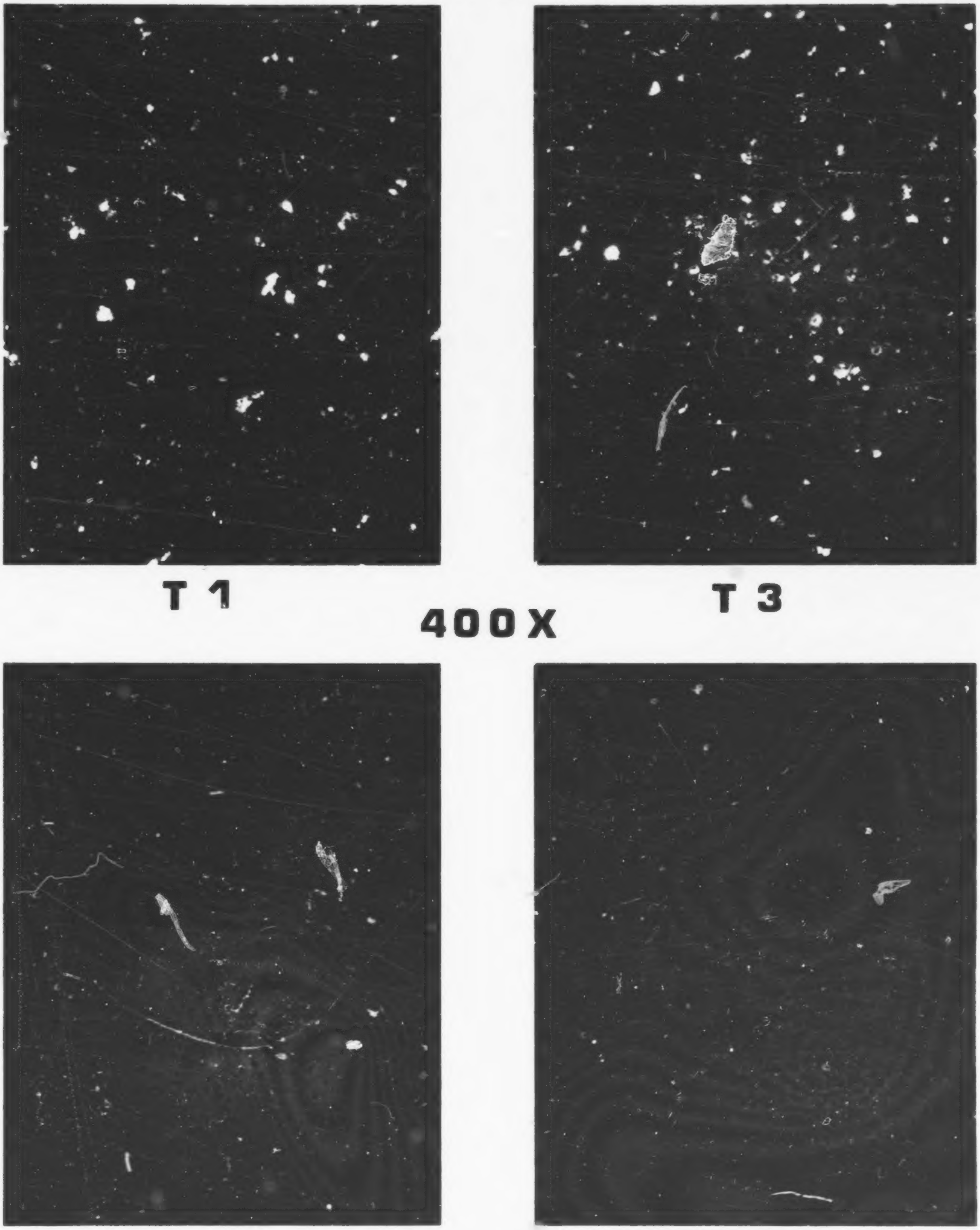
400 X

T 3

T 6

M

Figure 33. Exhaust Particulate on Andersen Plates by TEM - From Run #13



T 1

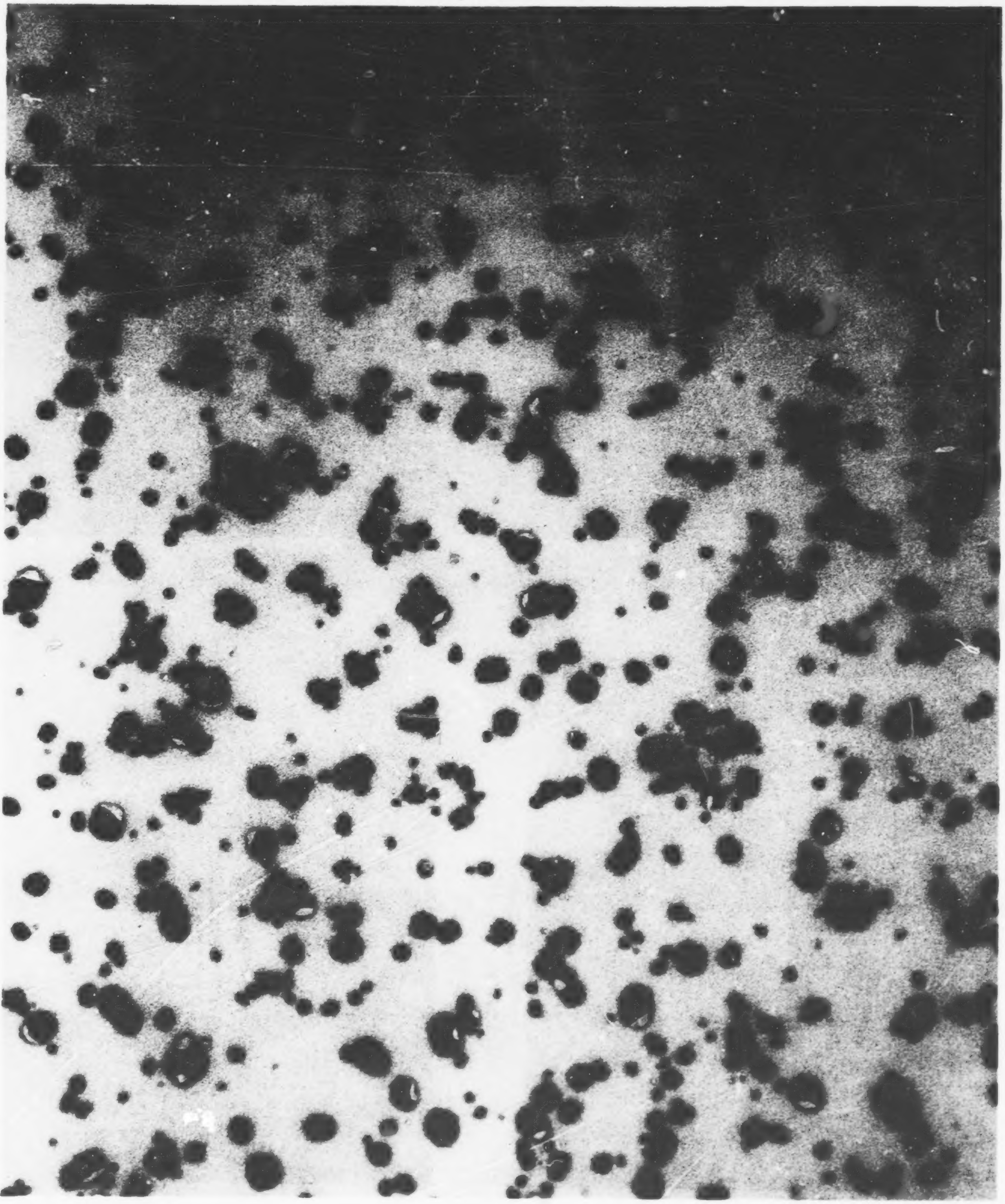
T 3

400 X

T 6

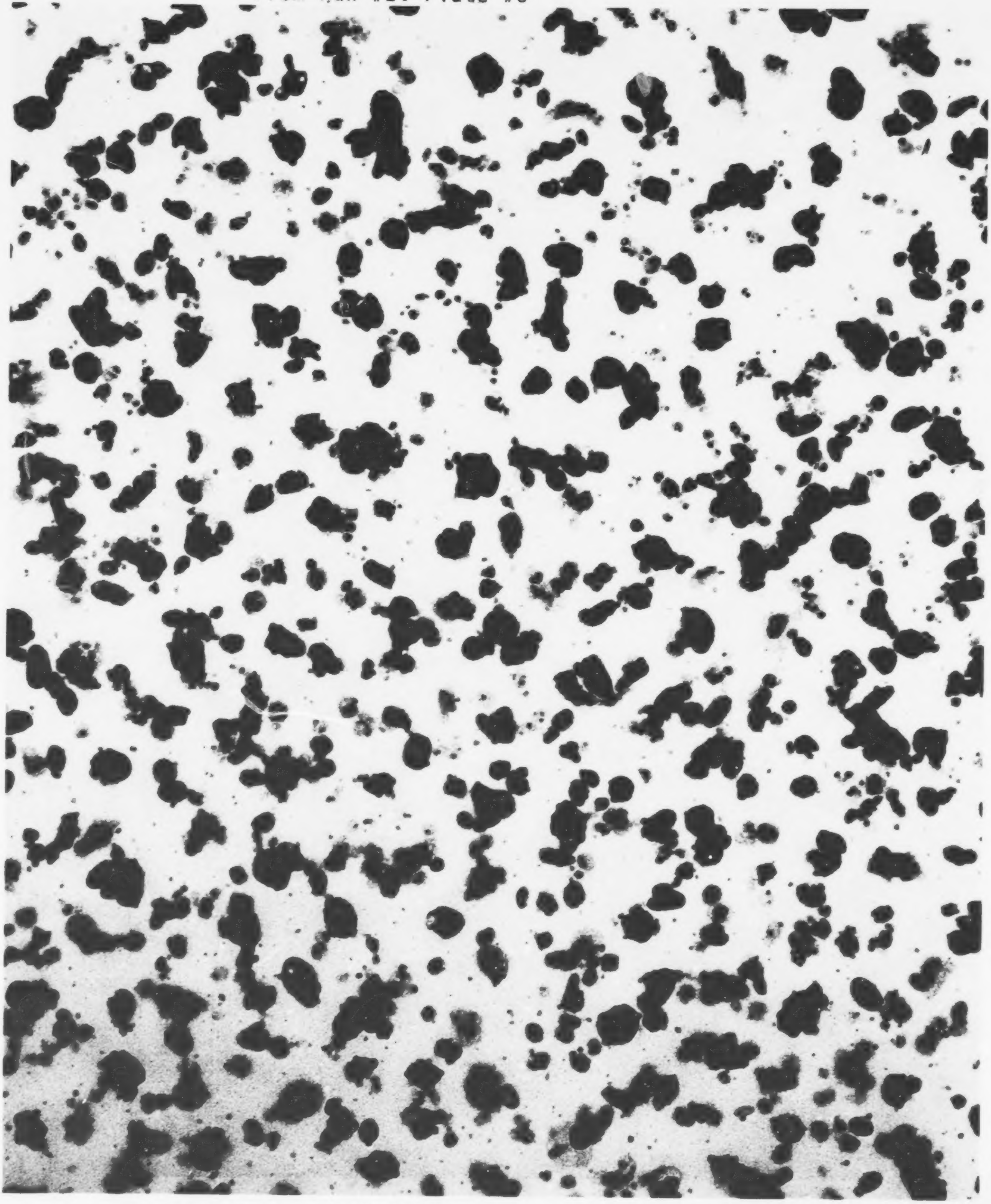
M

Figure 34. Exhaust Particulate on Andersen Plates by TEM - From Run #2, Plate #1



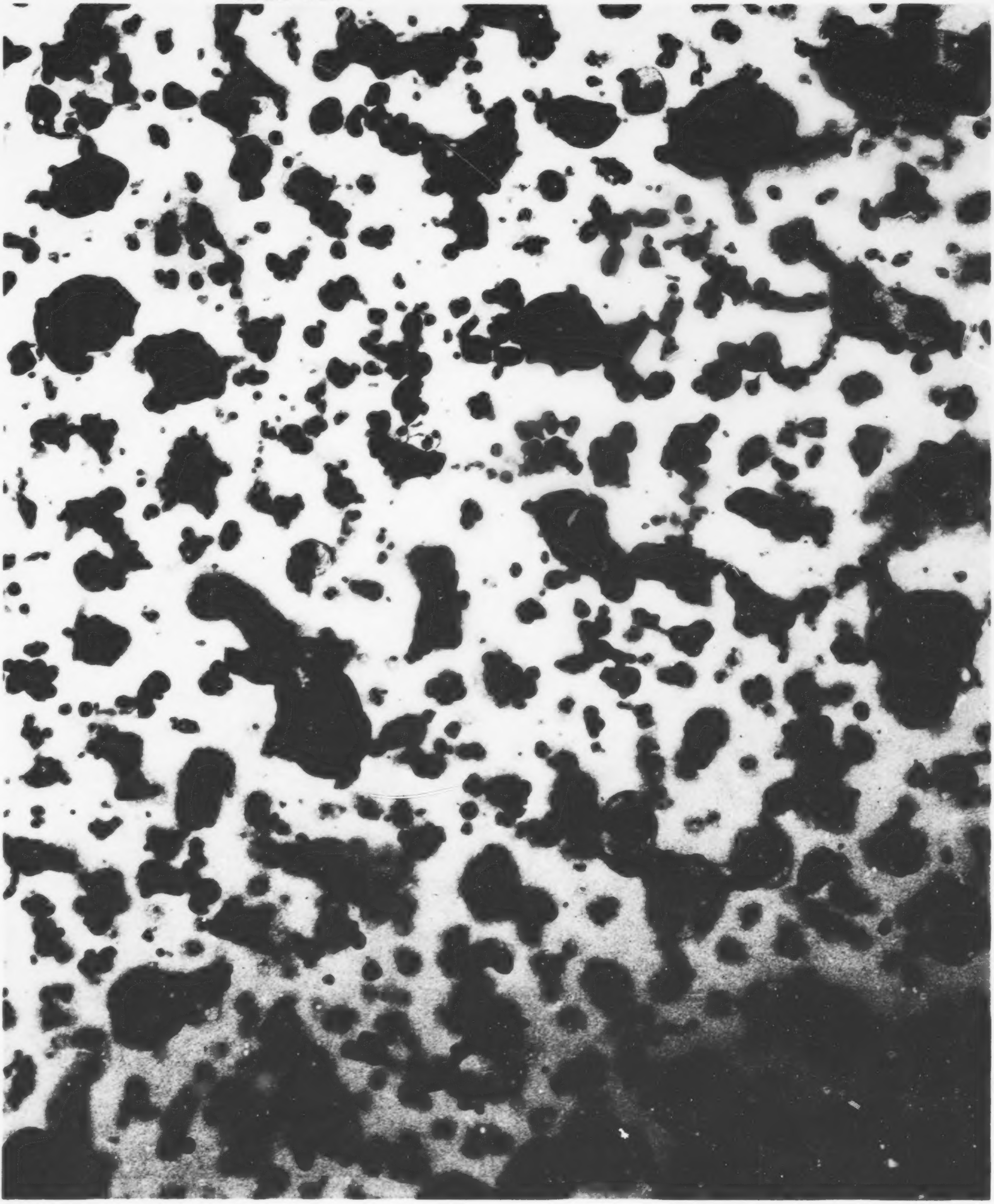
Magnification - 119,700x

Figure 35. Exhaust Particulate on Andersen Plates by TEM - From Run #2. Plate #6



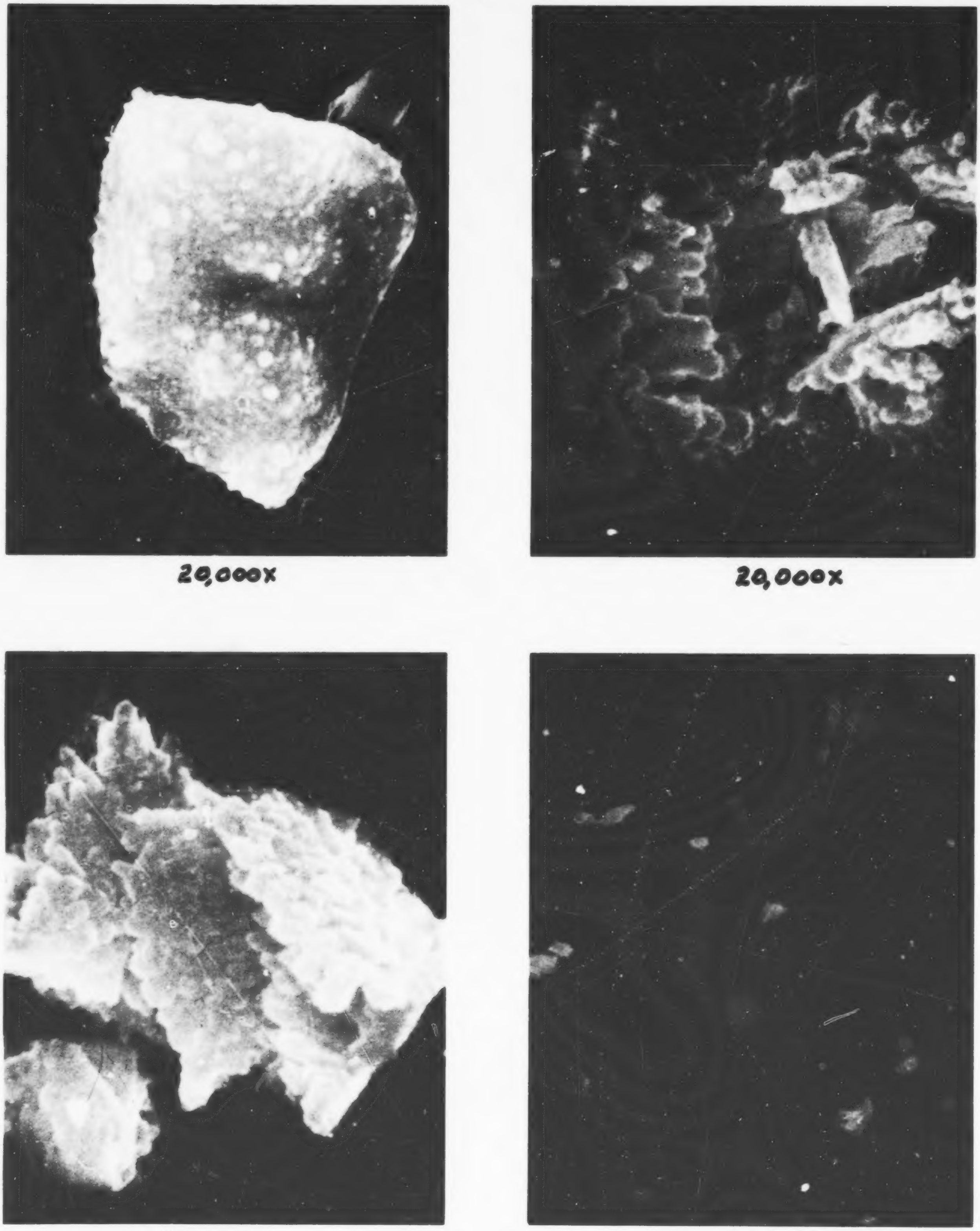
Magnification - 119,700x

Figure 36. Exhaust Particulate on Millipore Filter by TEM - From Run #2



Magnification - 119,700x

Figure 37. Exhaust Particulate on Andersen Plates by SEM - From Run #1



20,000x

20,000x

20,000X

1,000X

Figure 38. Exhaust Particulate on Andersen Plates by SEM - From Run #2

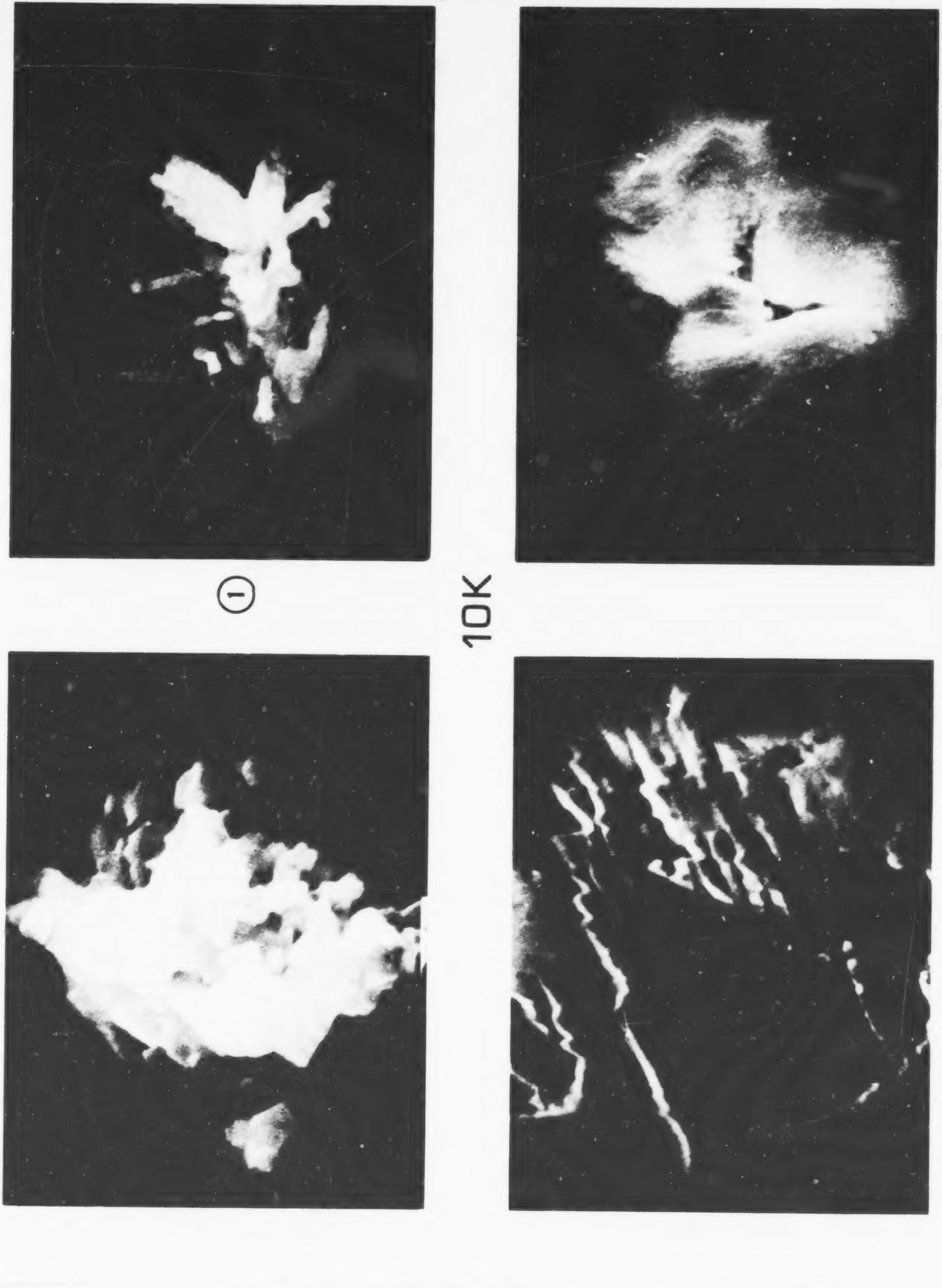


Figure 39. Exhaust Particulate on Andersen Plates by SEM - From Run #2, Plate #6

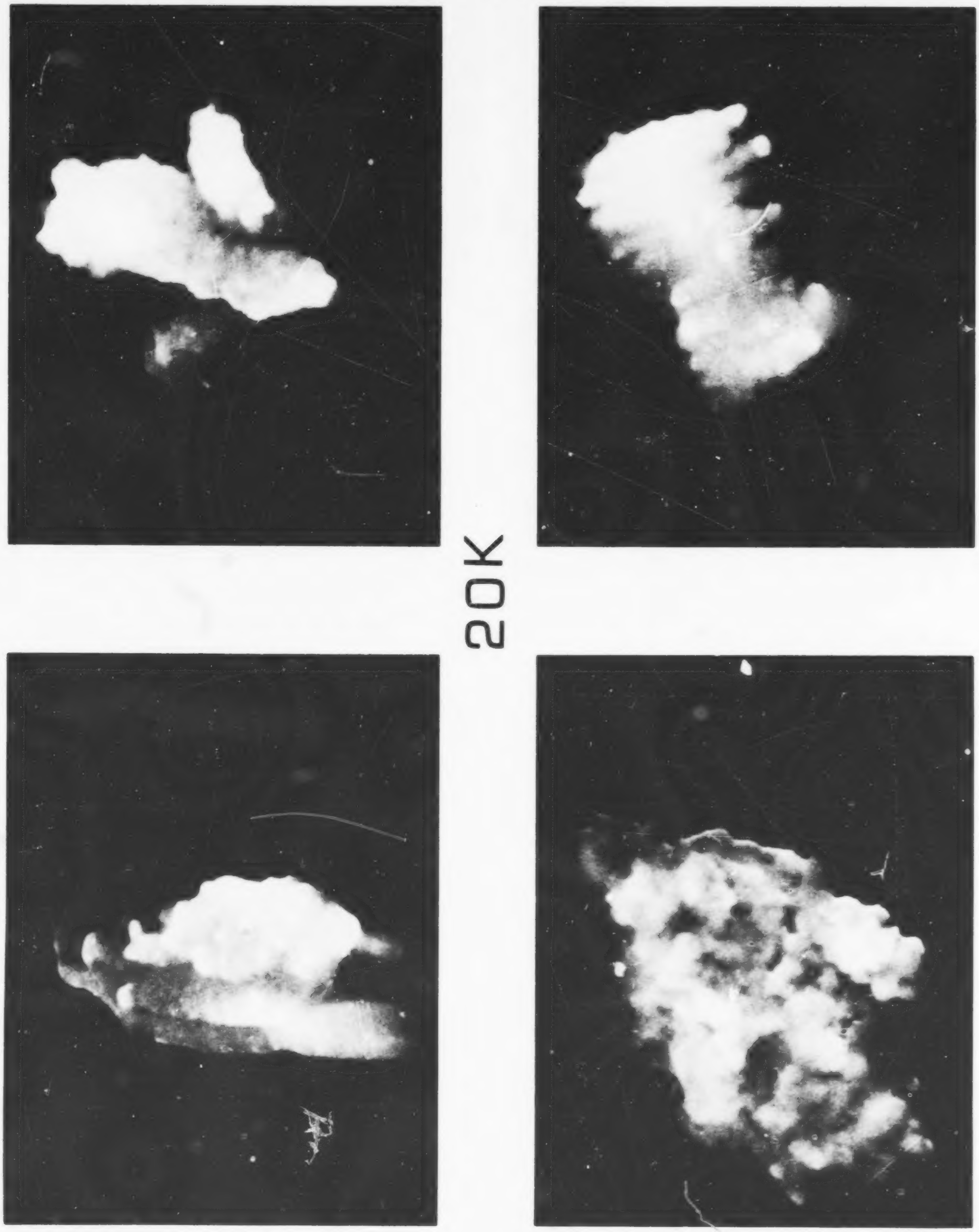


Figure 40. Exhaust Particulate on Andersen Plates by SEM - From Run #2, Plate #1

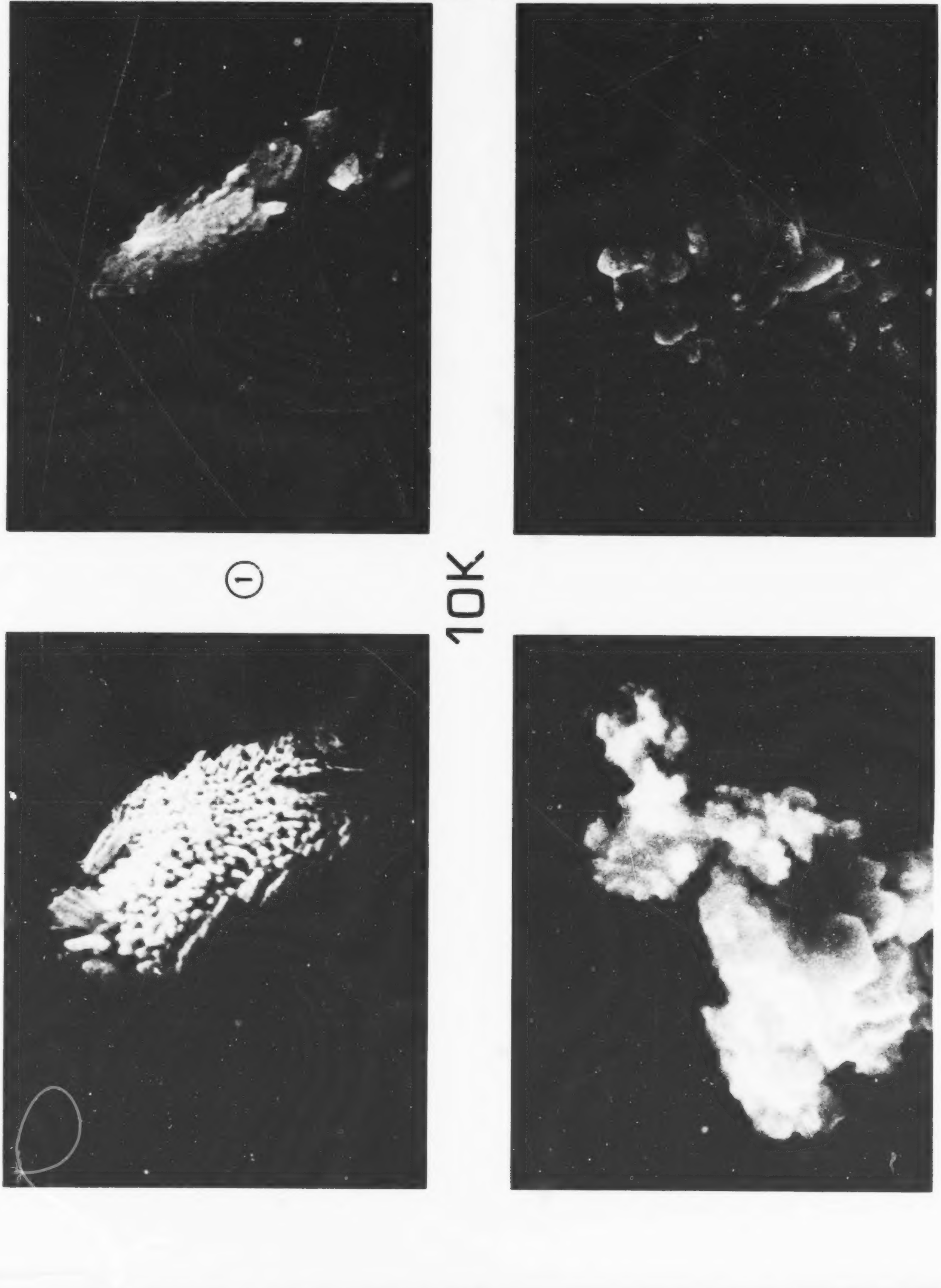
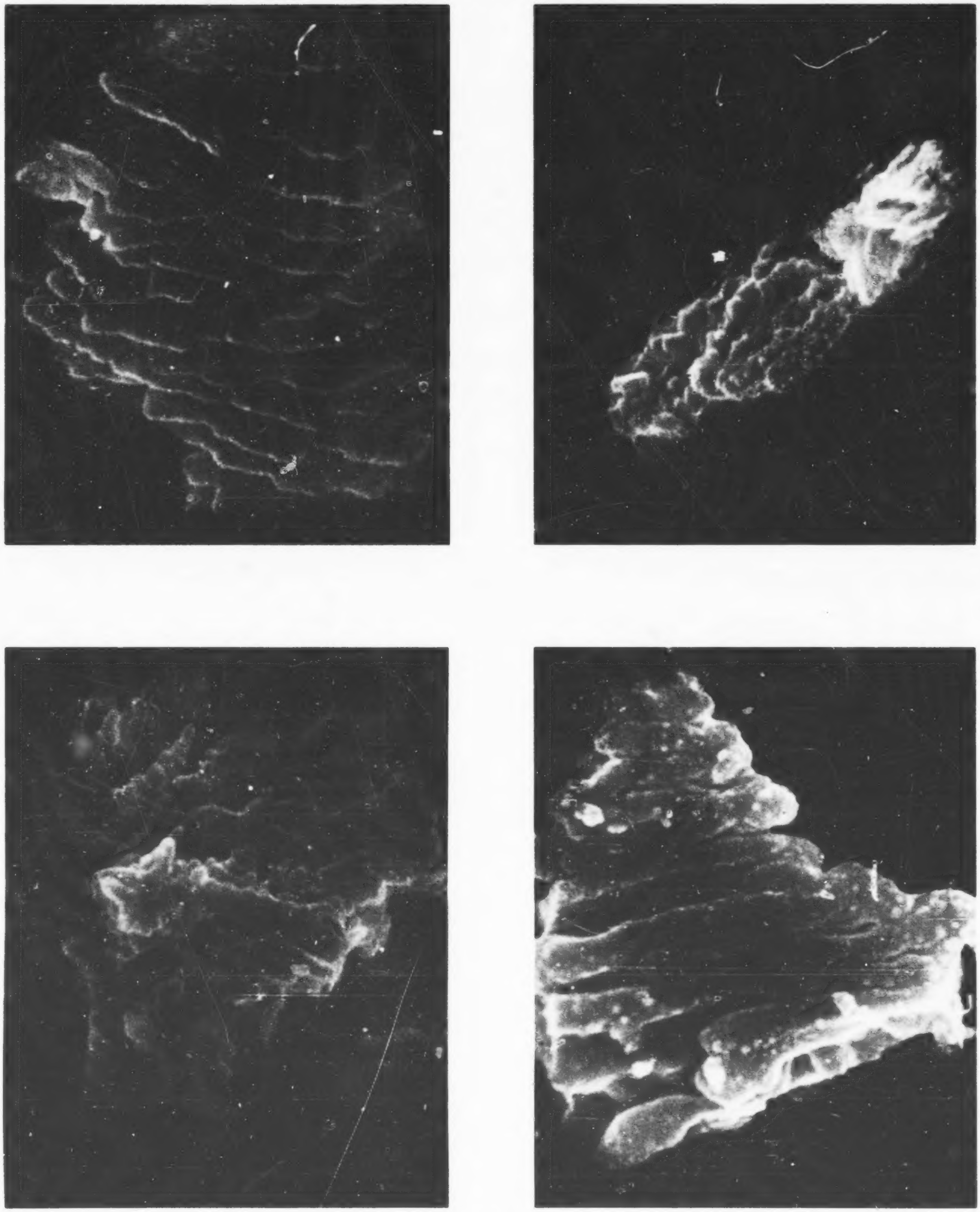
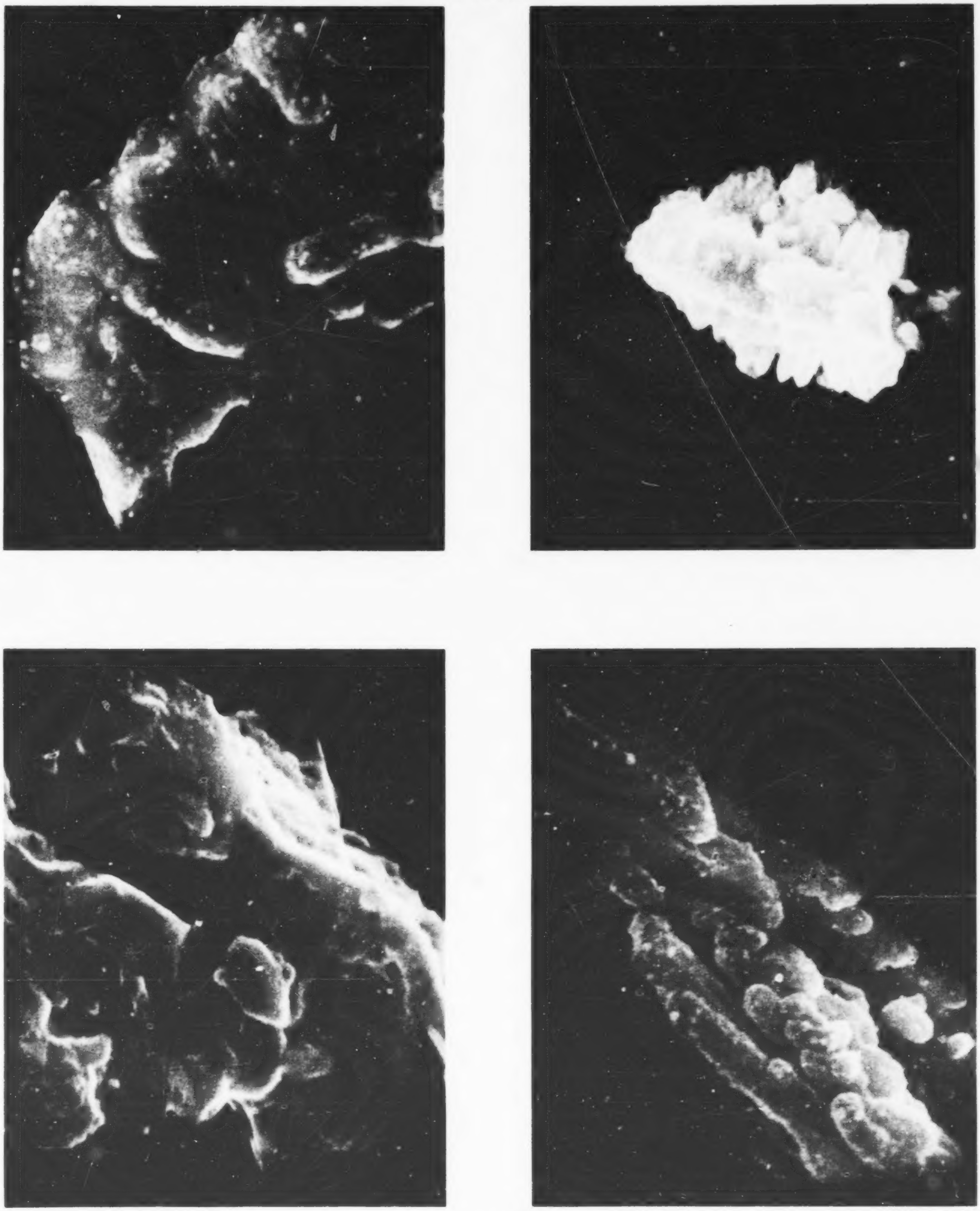


Figure 41. Exhaust Particulate on Andersen Plates by SEM - From Run #1, Plate #1



Magnification - 10,000x

Figure 42. Exhaust Particulate on Andersen Plates by SEM - From Run #1, Plate #1



Magnification - 10,000x

Figure 43. Exhaust Particulate on Andersen Plates by SEM - From Run #21, Plate #1

GR-21-1

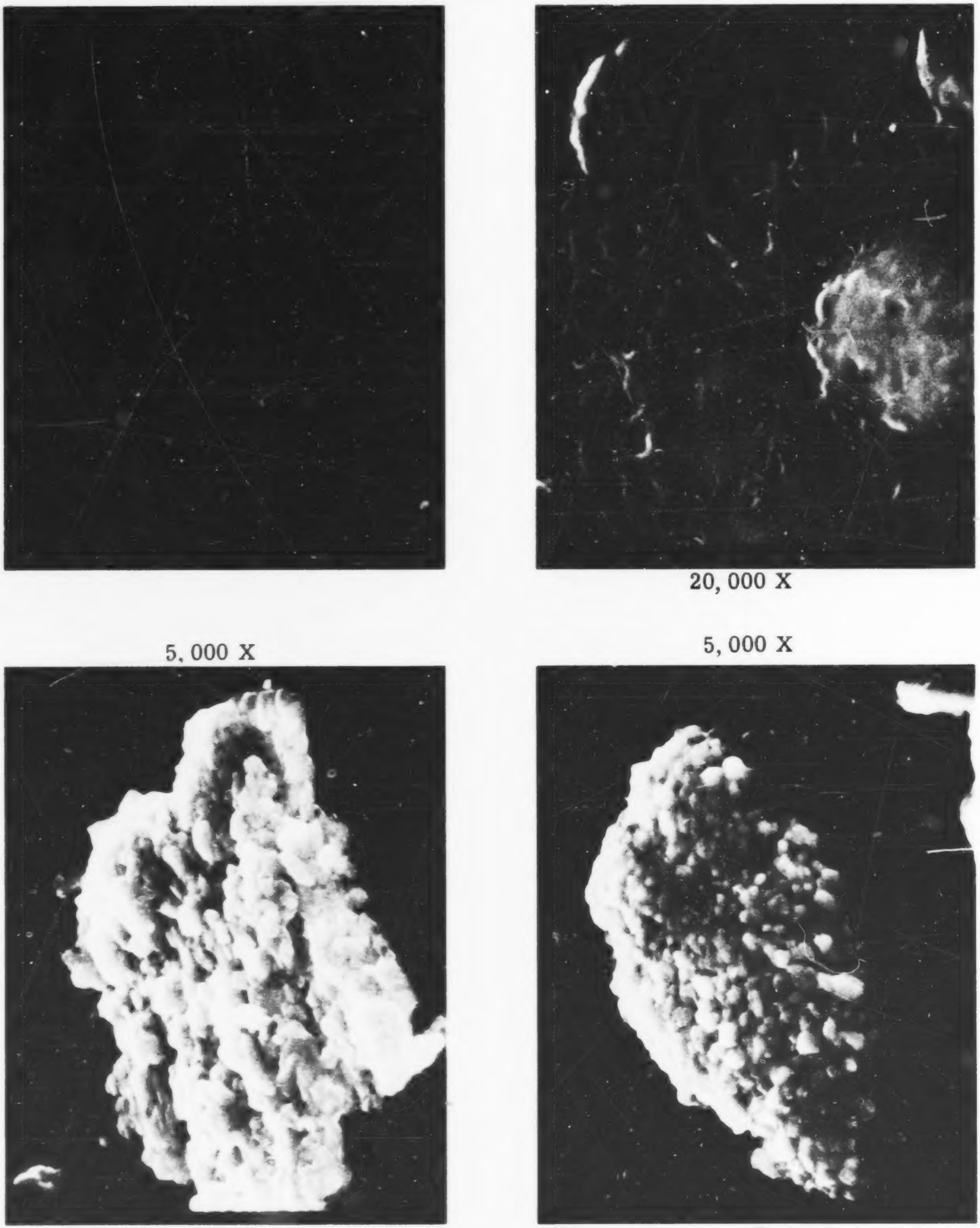

20, 000 X
5, 000 X
5, 000 X
C
D

Figure 44. Exhaust Particulate on Andersen Plates by SEM - From Run #21, Plate #1

GR-21-2

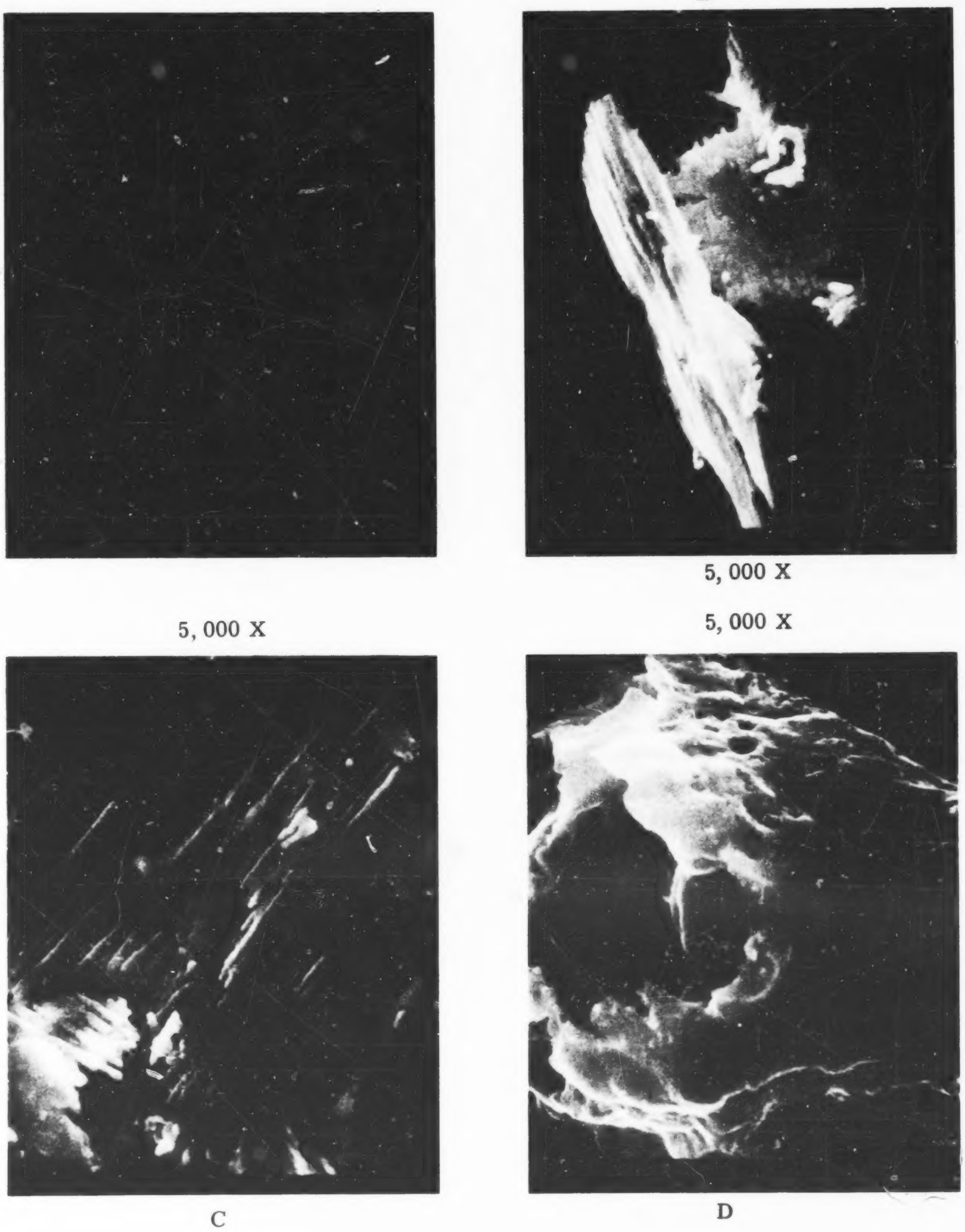
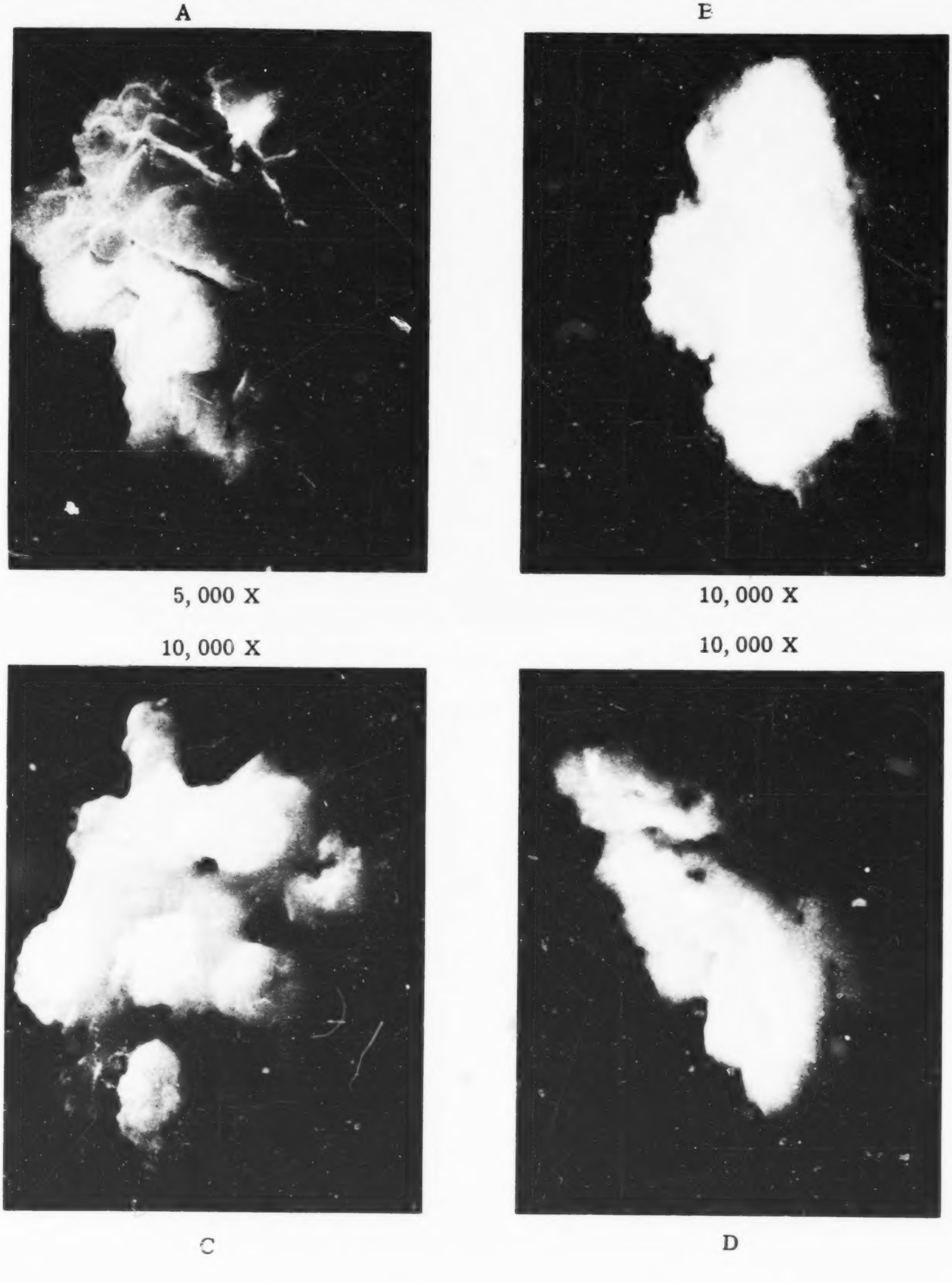

B
5, 000 X
5, 000 X
5, 000 X
C
D

Figure 45. Exhaust Particulate on Andersen Plates by SEM - From Run #42, Plates 1, 4, and 7

GR-42-1


A
B
5,000 X
10,000 X
10,000 X
10,000 X
C
D

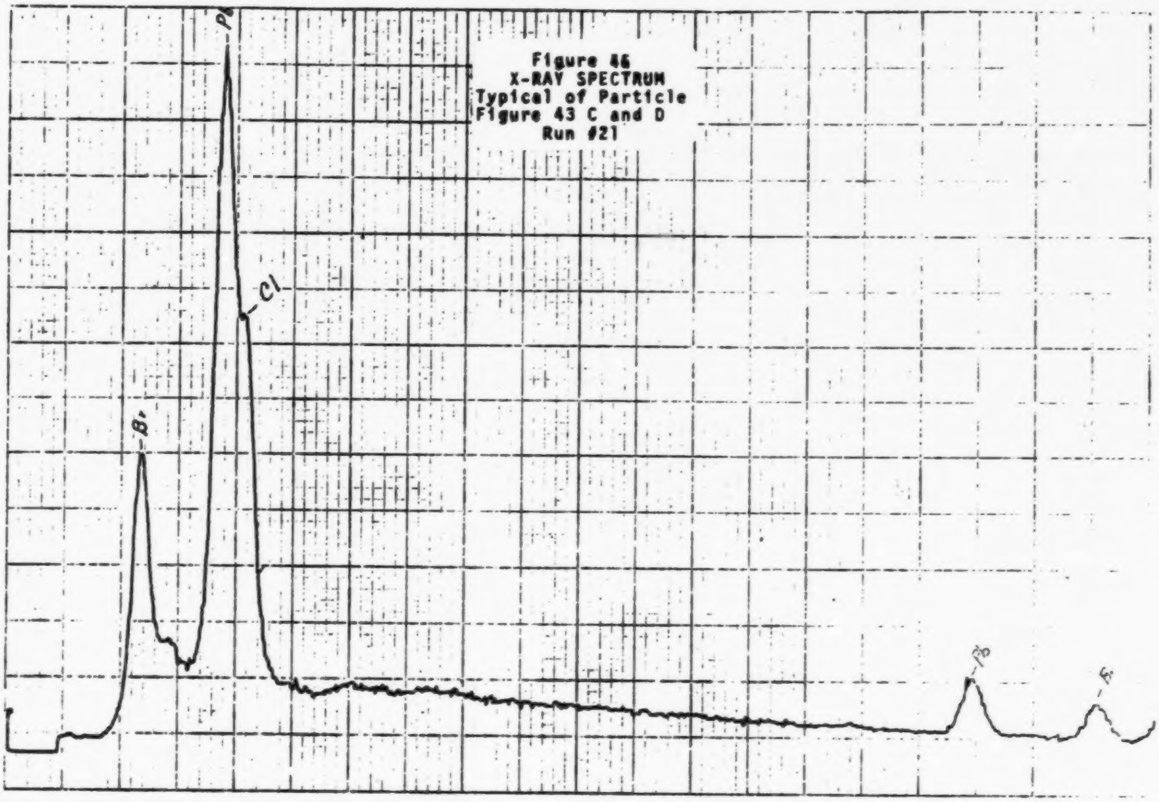


Figure 46
X-RAY SPECTRUM
Typical of Particle
Figure 43 C and D
Run #21

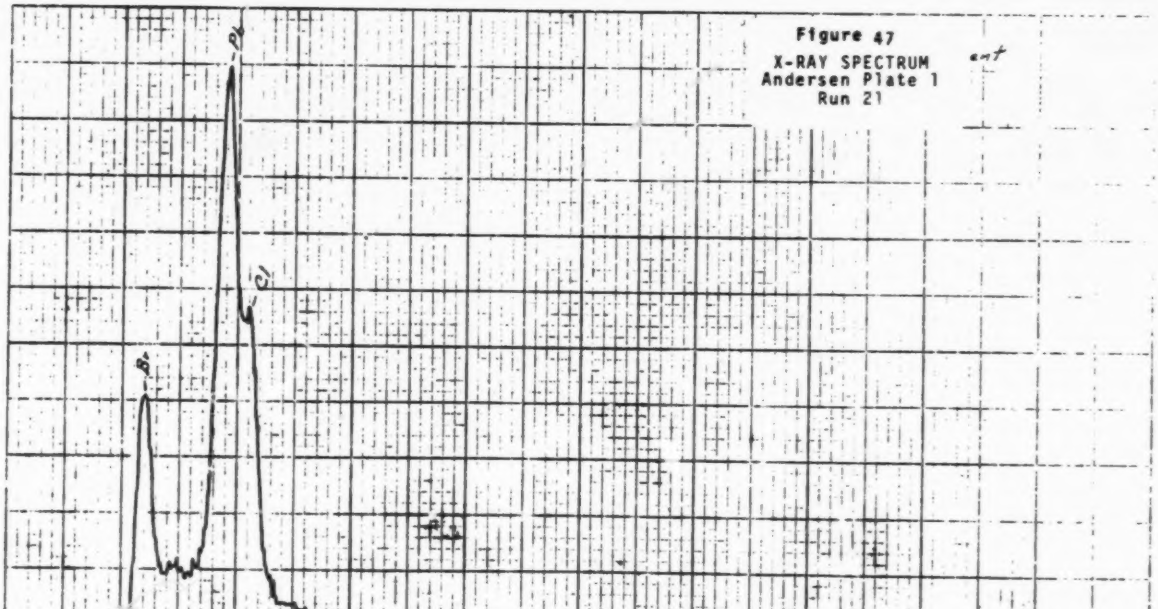


Figure 47
X-RAY SPECTRUM
Andersen Plate 1
Run 21

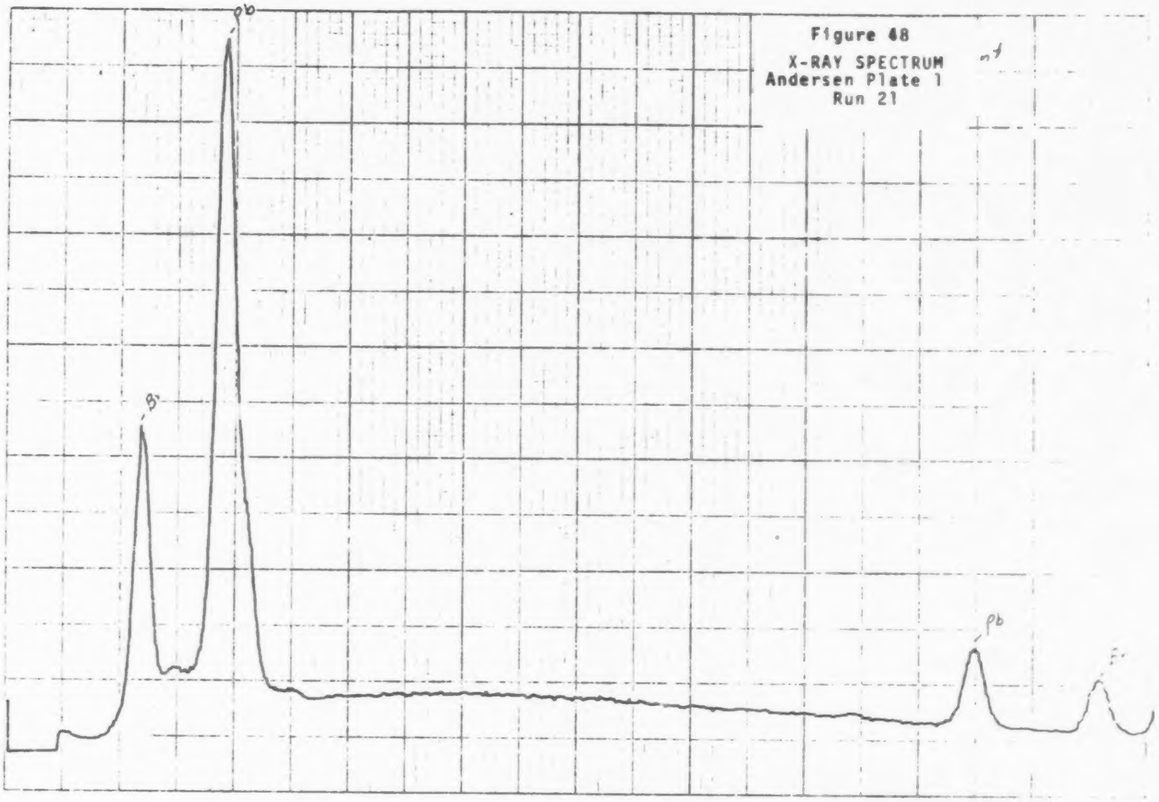


Figure 48

X-RAY SPECTRUM
Andersen Plate 1
Run 21

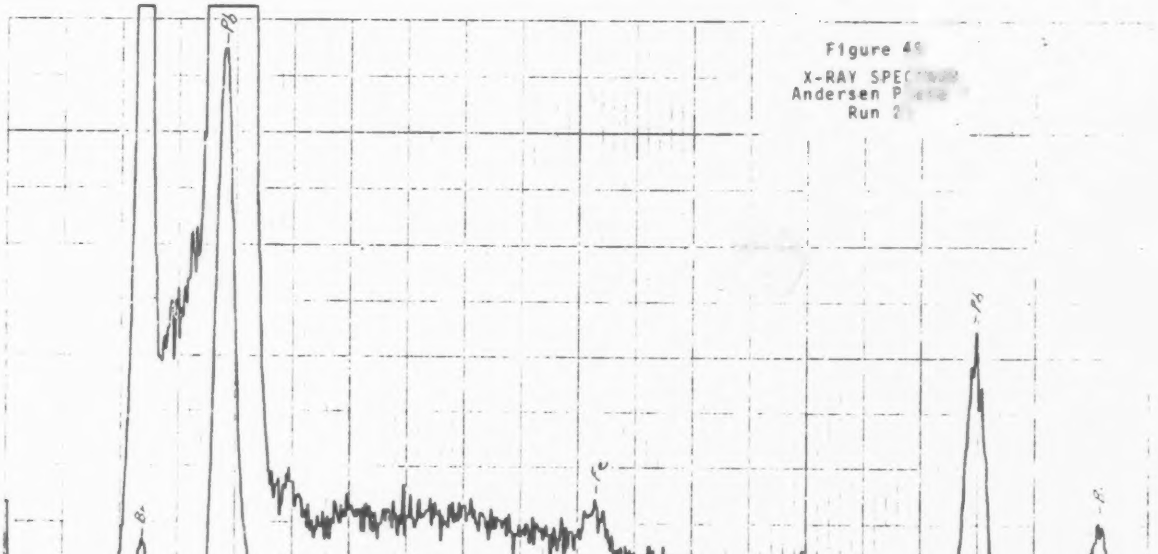


Figure 49

X-RAY SPECTRUM
Andersen Plate [illegible]
Run 21

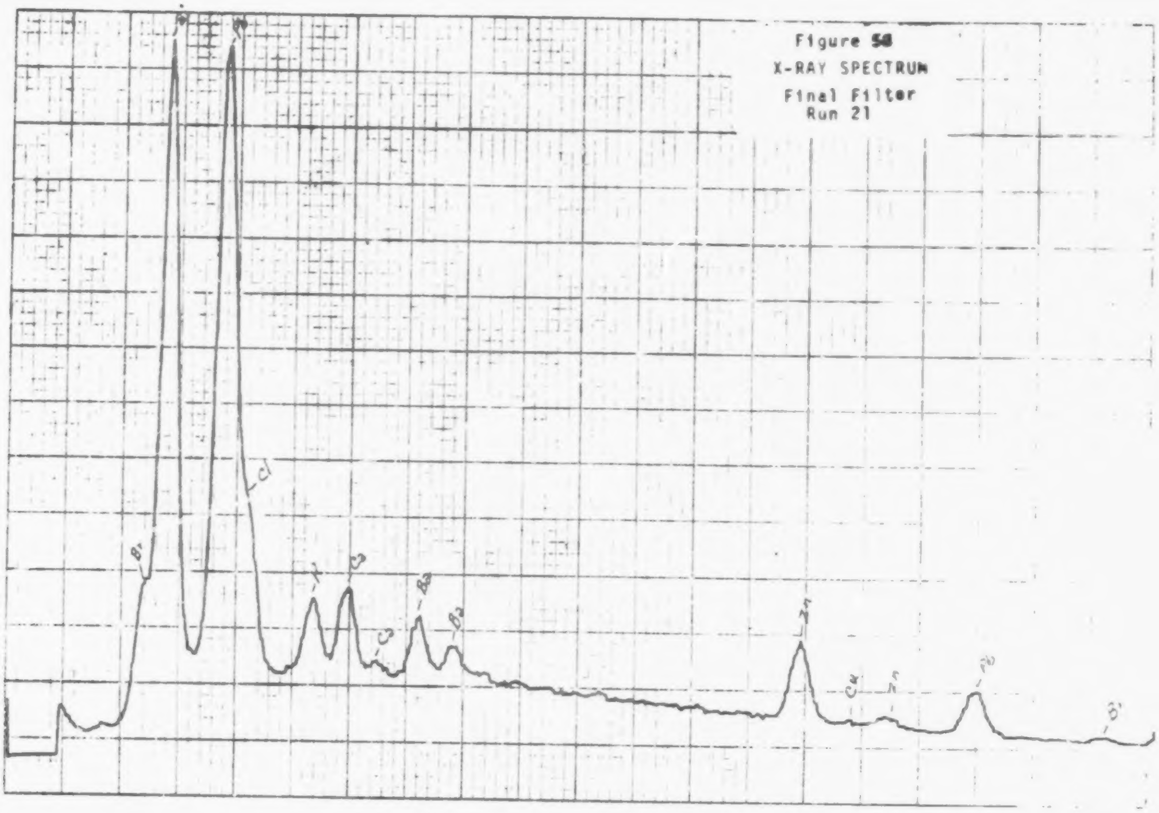


Figure 50

X-RAY SPECTRUM

Final Filter
Run 21

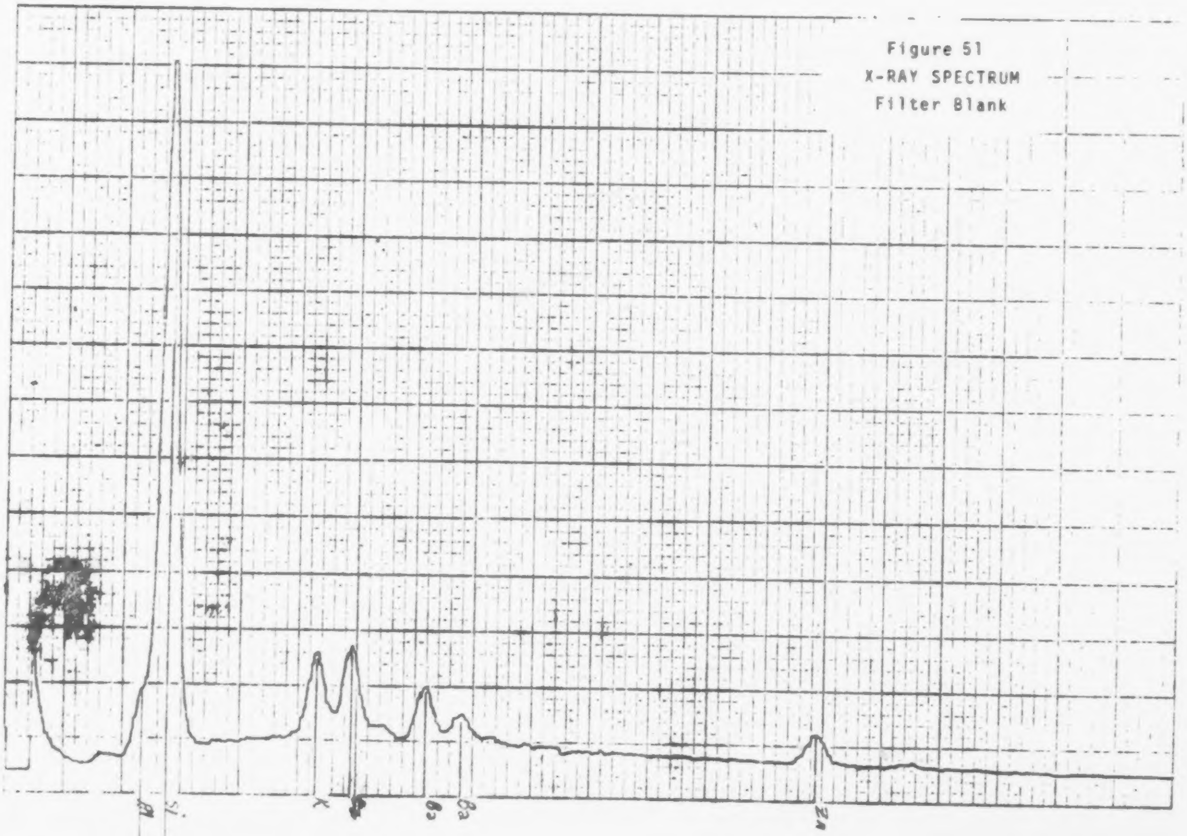


Figure 51

X-RAY SPECTRUM

Filter Blank

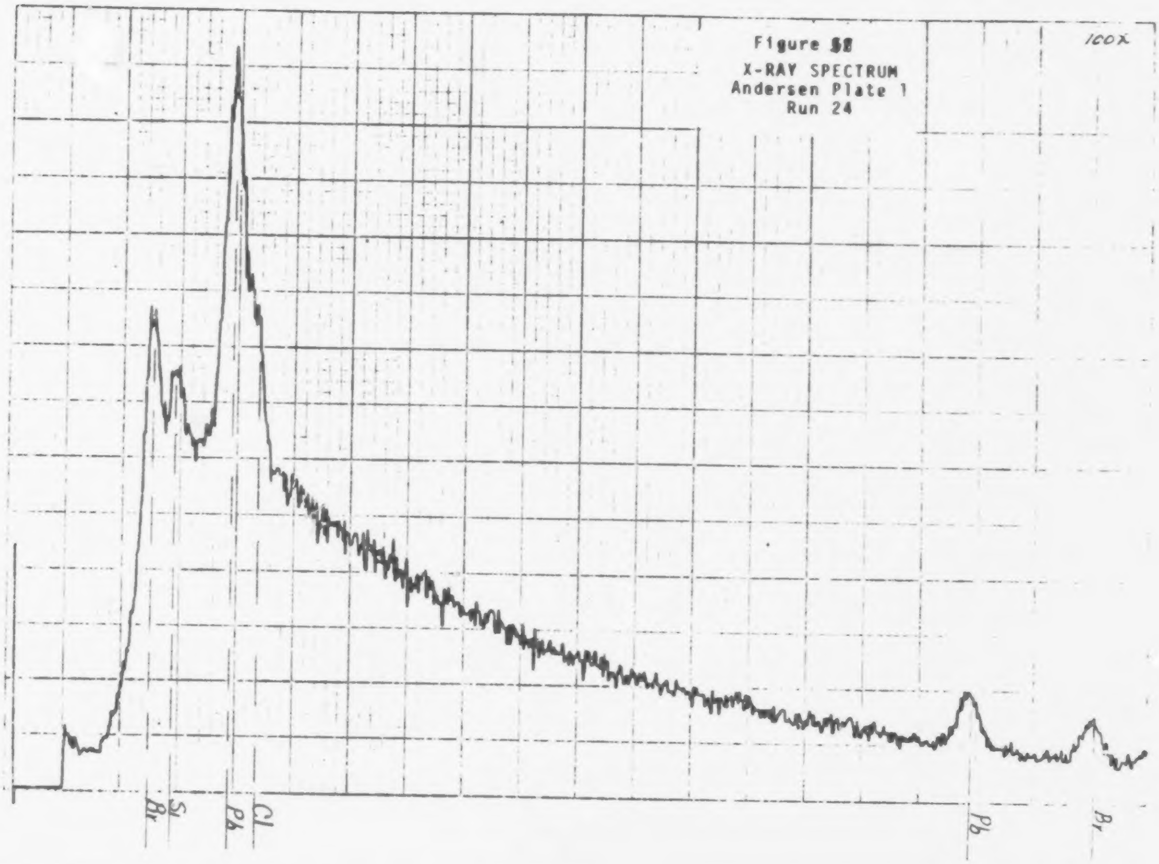


Figure 52
X-RAY SPECTRUM
Andersen Plate 1
Run 24

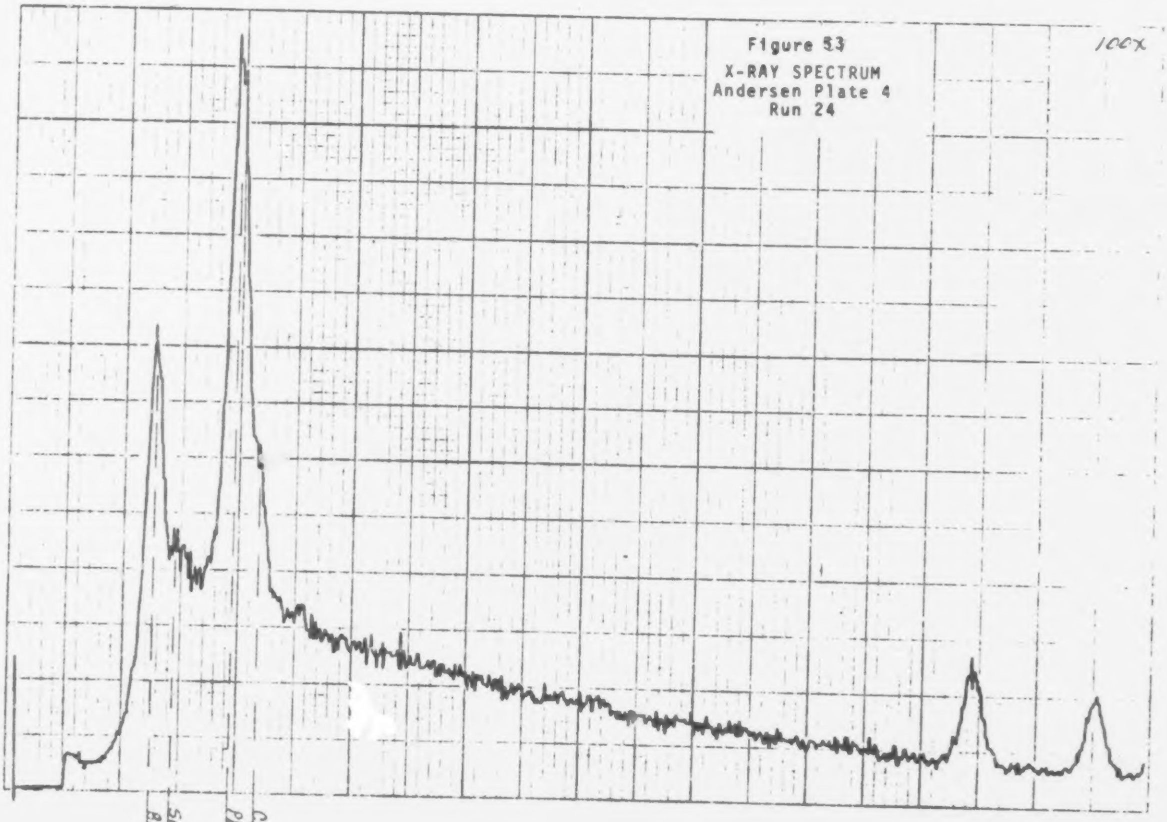


Figure 53
X-RAY SPECTRUM
Andersen Plate 4
Run 24

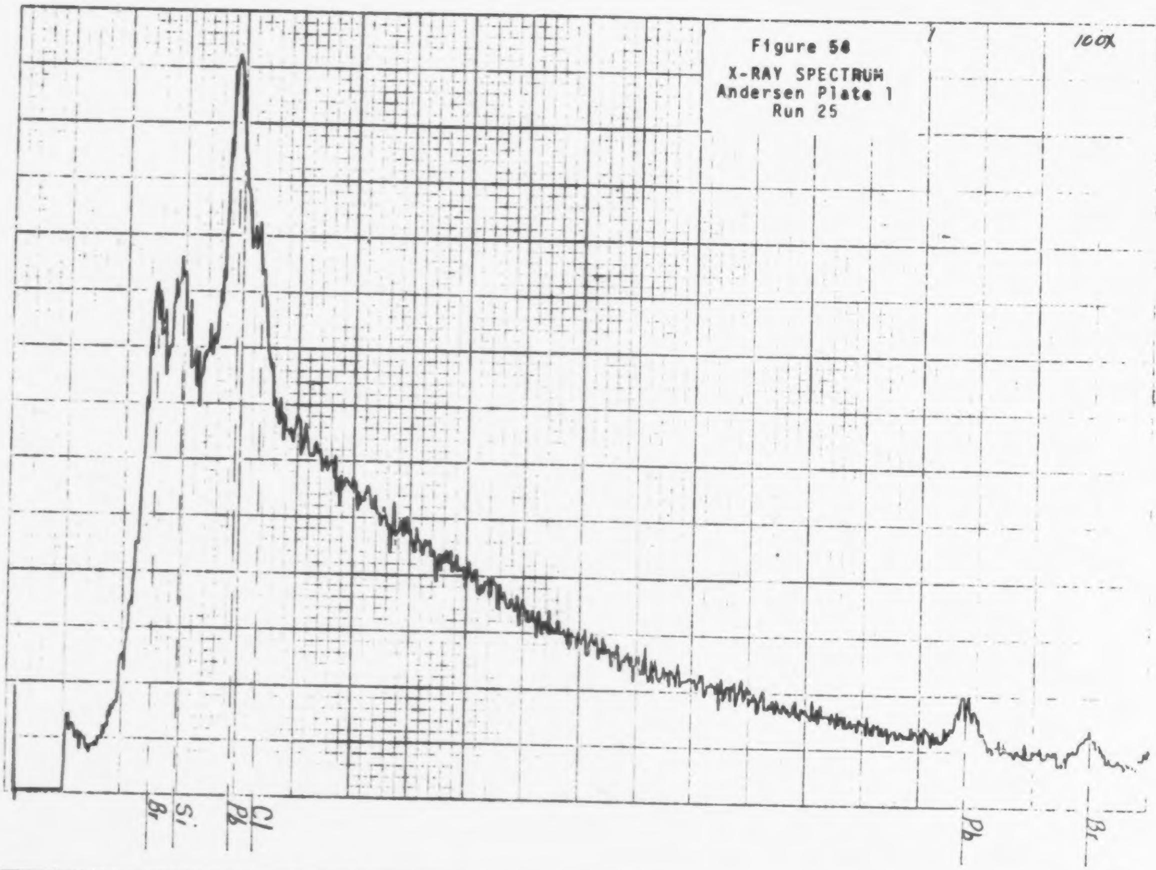


Figure 54

X-RAY SPECTRUM
Andersen Plate 1
Run 25

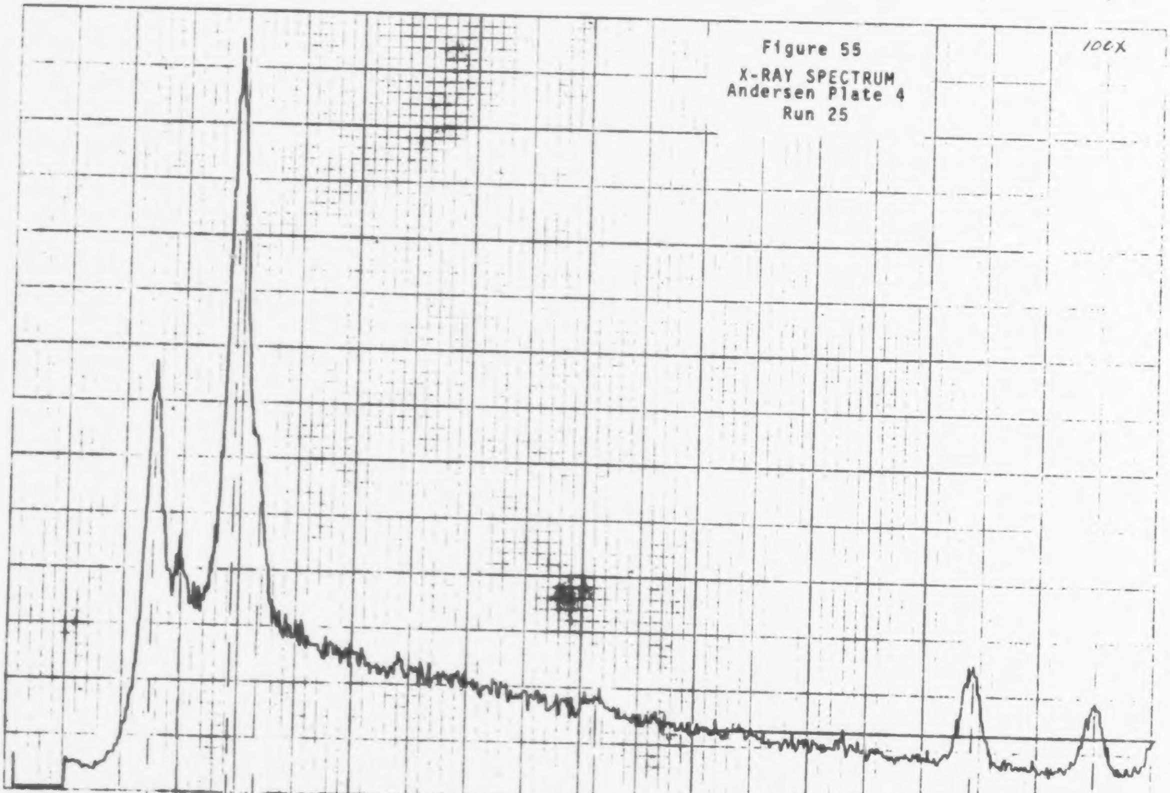


Figure 55

X-RAY SPECTRUM
Andersen Plate 4
Run 25

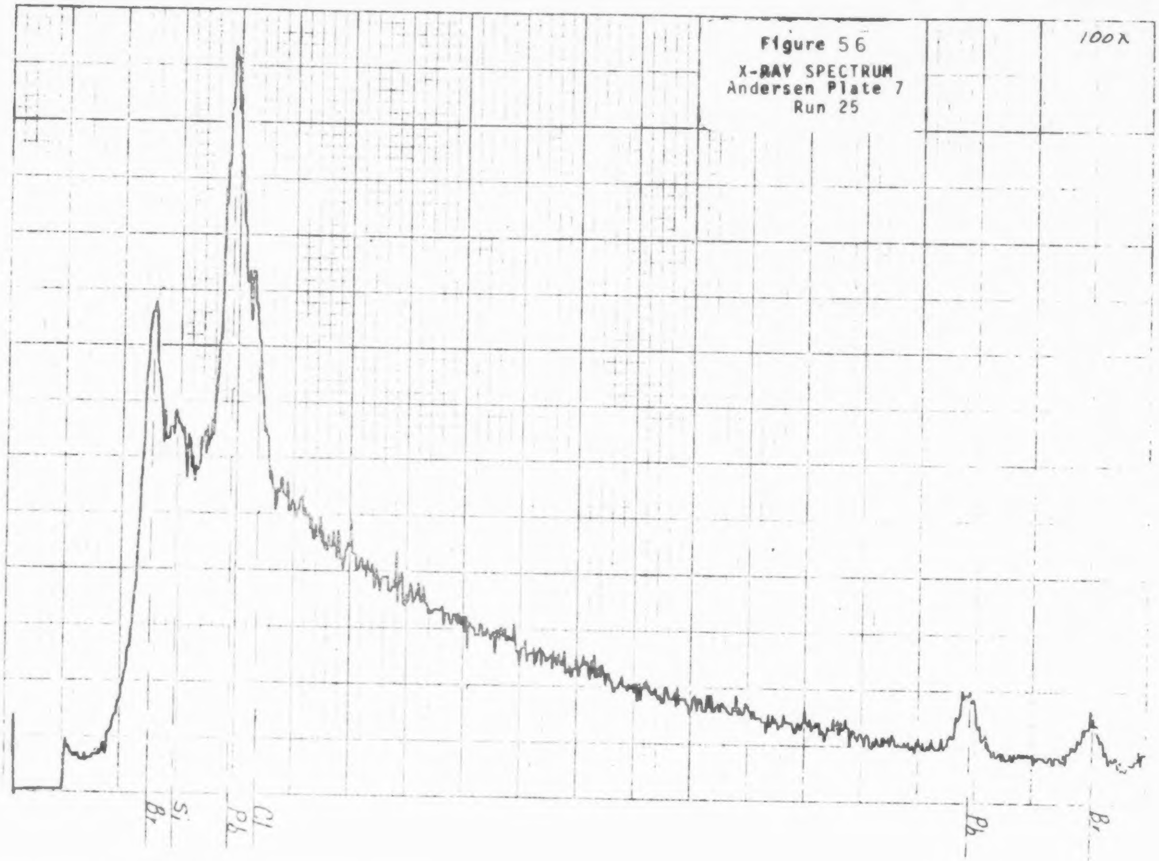


Figure 56

X-RAY SPECTRUM
Andersen Plate 7
Run 25

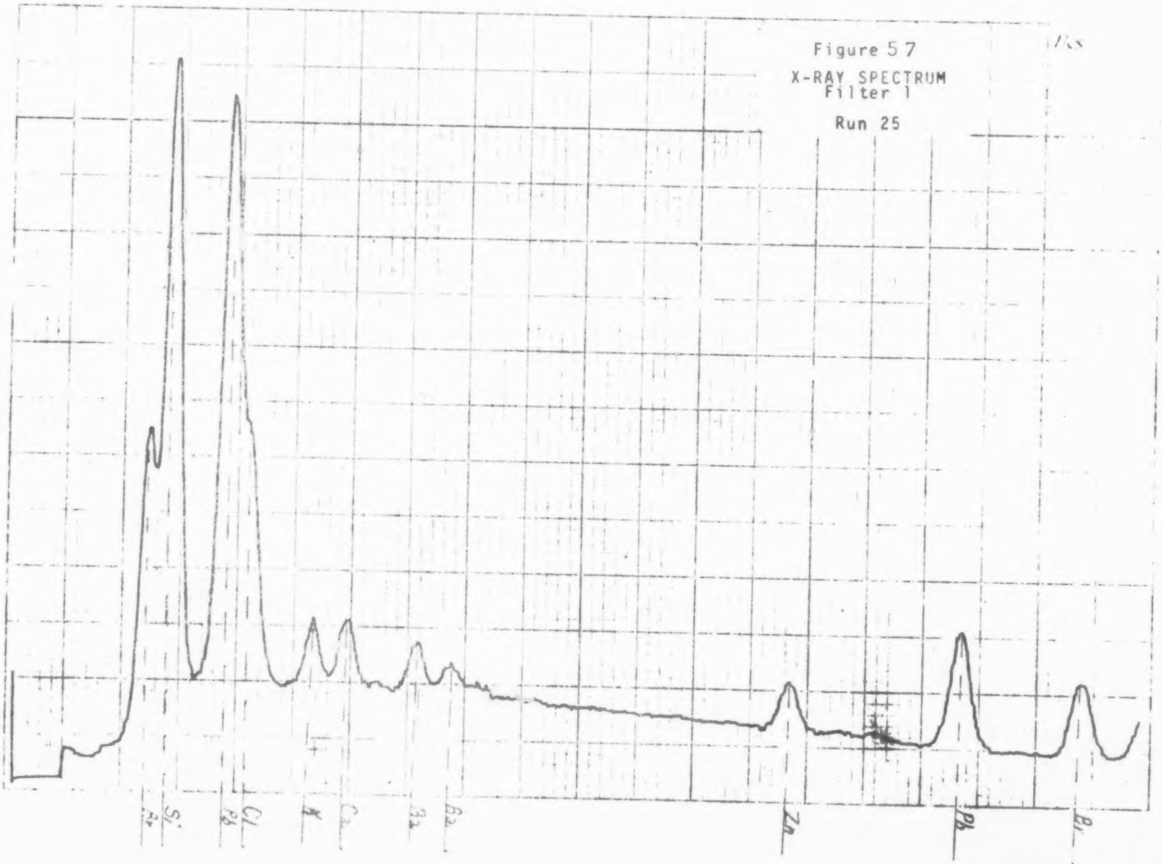


Figure 57

X-RAY SPECTRUM
Filter 1

Run 25

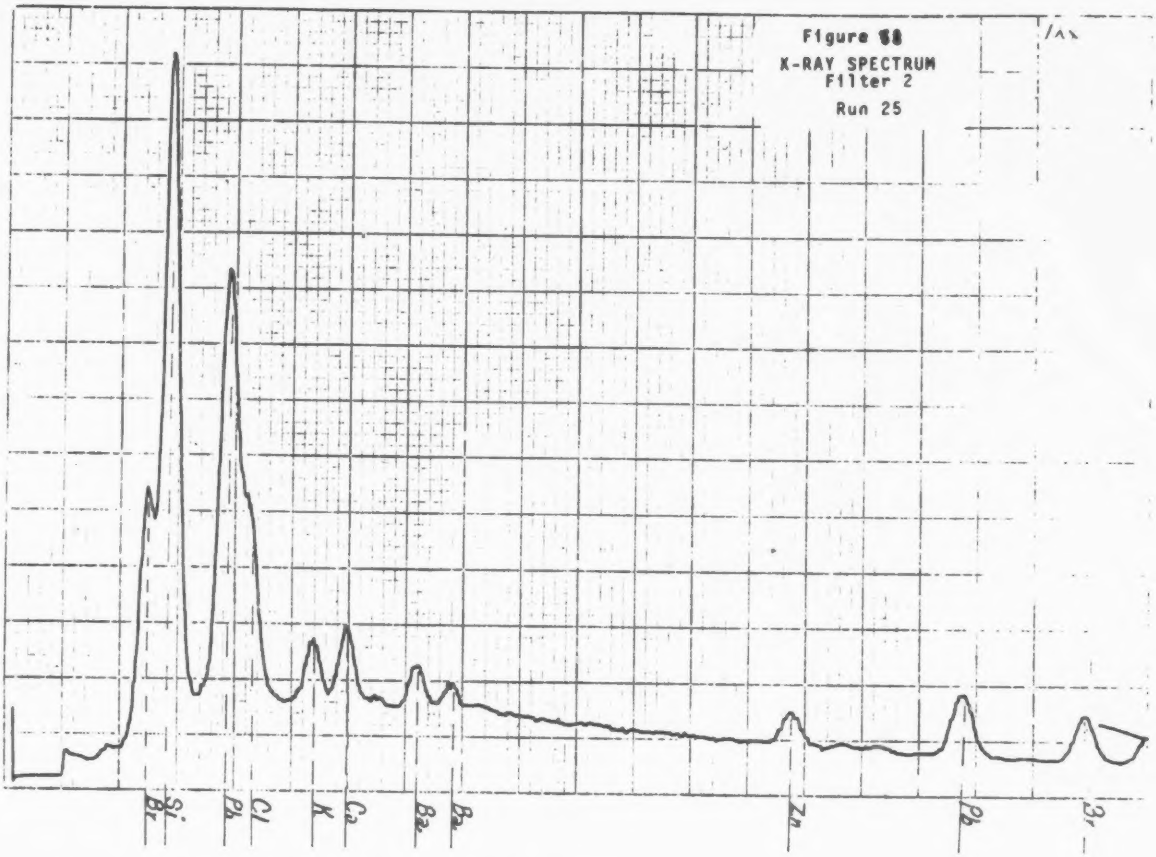


Figure 58

X-RAY SPECTRUM
Filter 2

Run 25

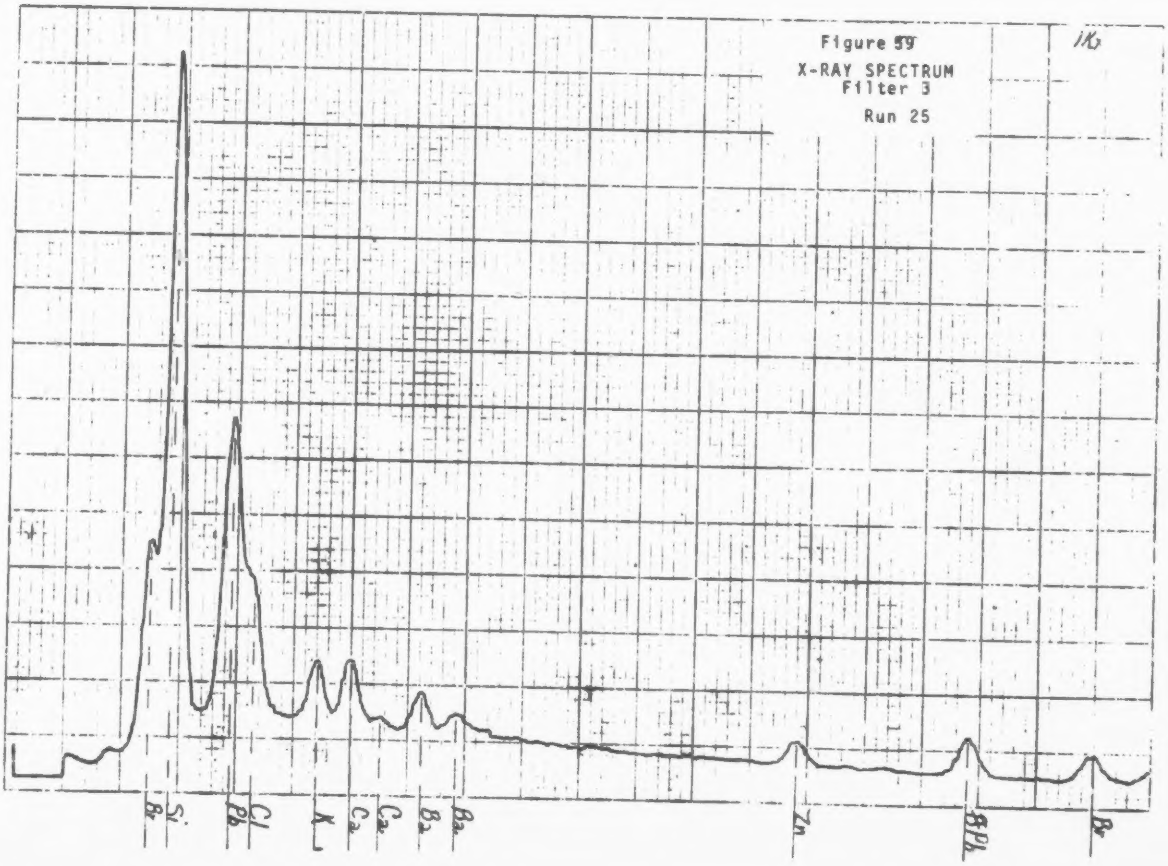


Figure 59

X-RAY SPECTRUM
Filter 3

Run 25

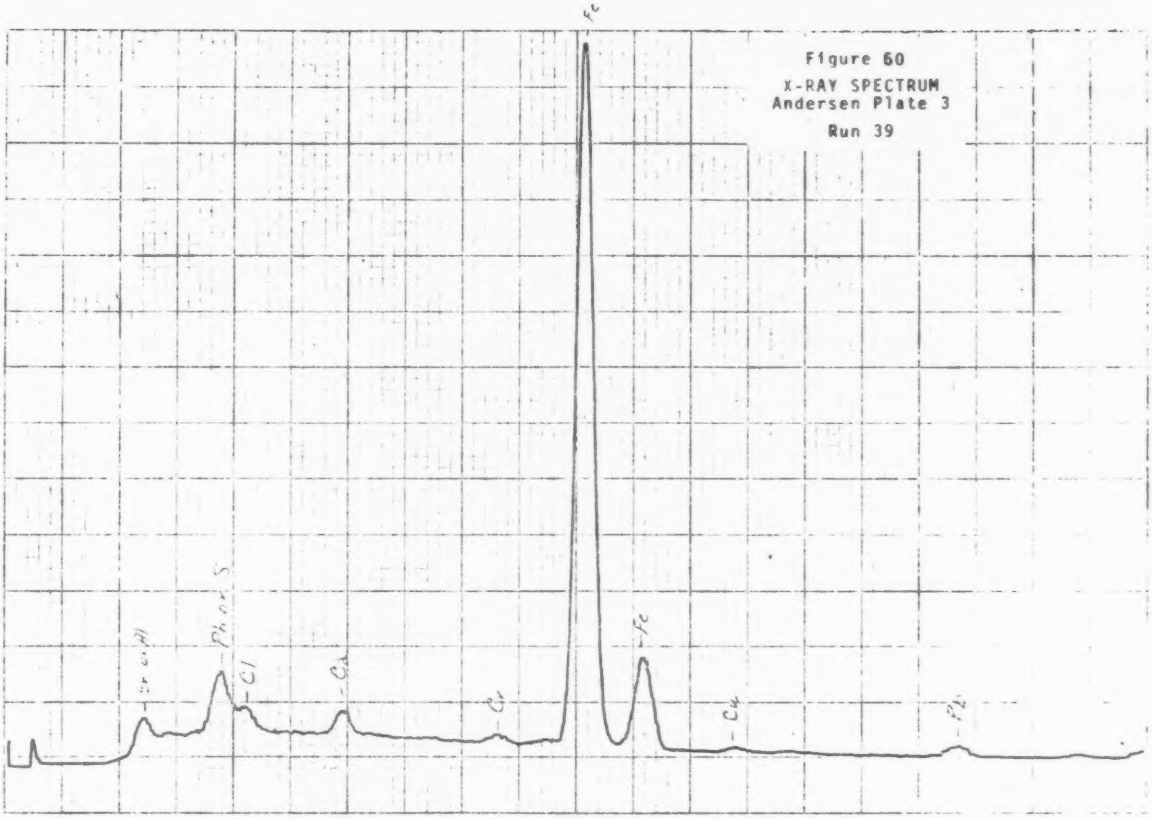


Figure 60
X-RAY SPECTRUM
Andersen Plate 3
Run 39

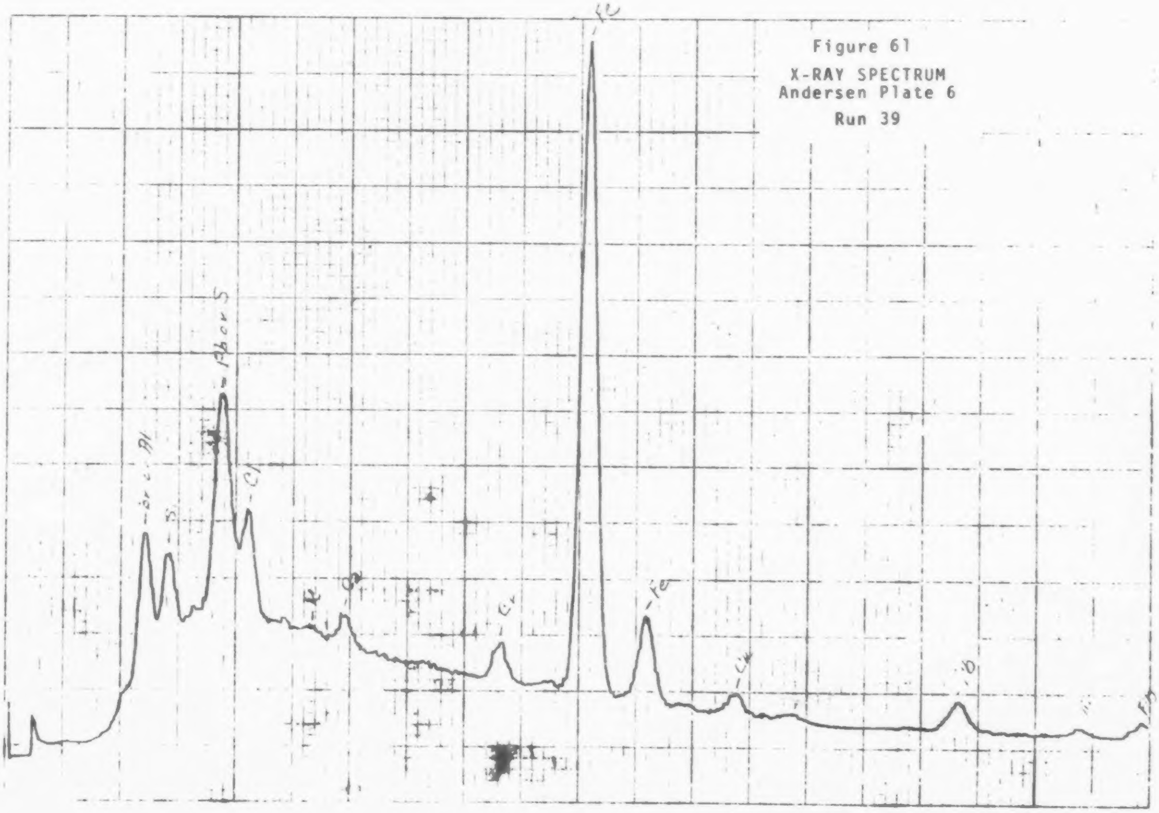


Figure 61
X-RAY SPECTRUM
Andersen Plate 6
Run 39

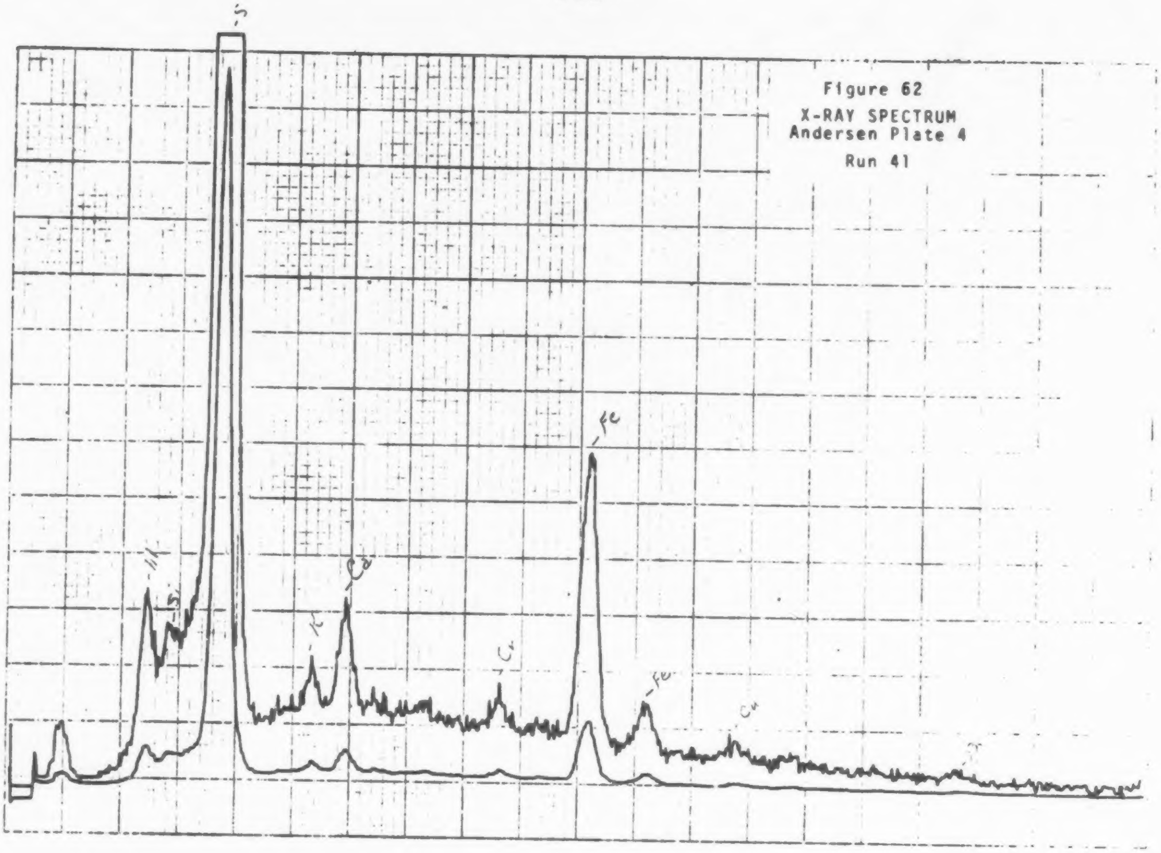


Figure 62
X-RAY SPECTRUM
Andersen Plate 4
Run 41

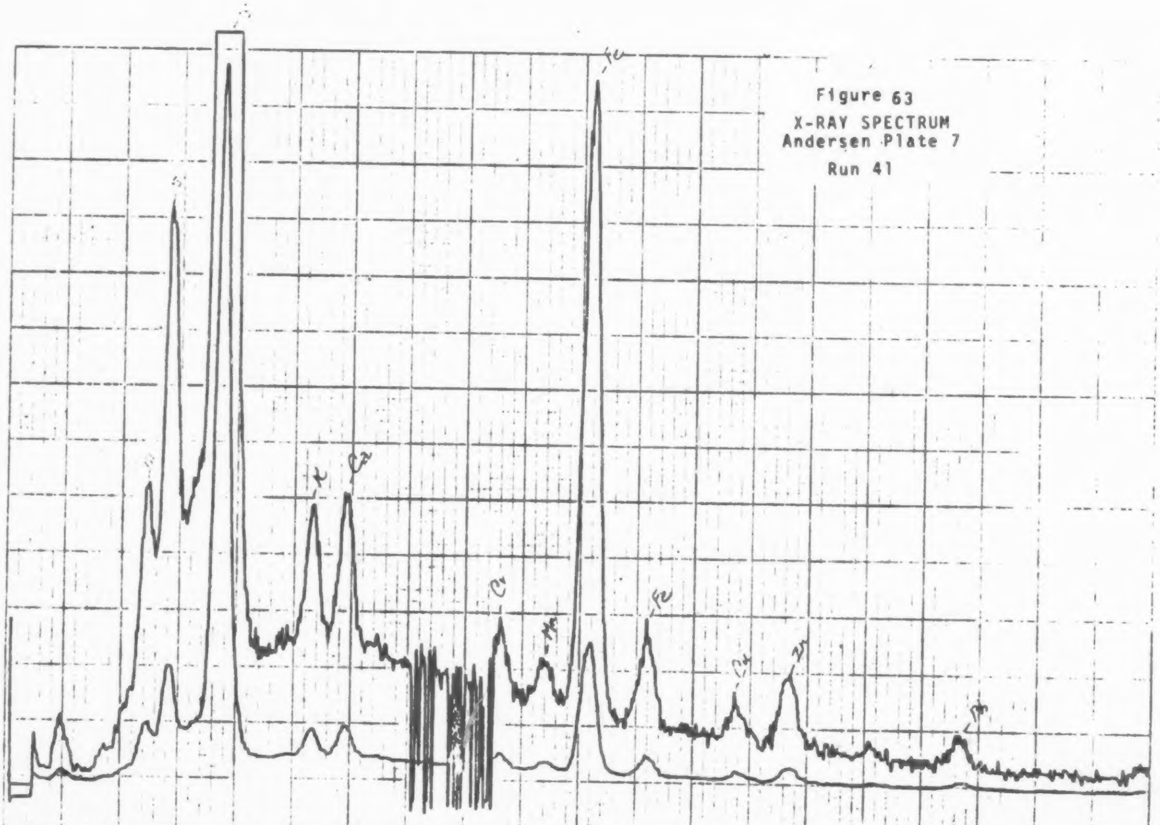


Figure 63
X-RAY SPECTRUM
Andersen Plate 7
Run 41

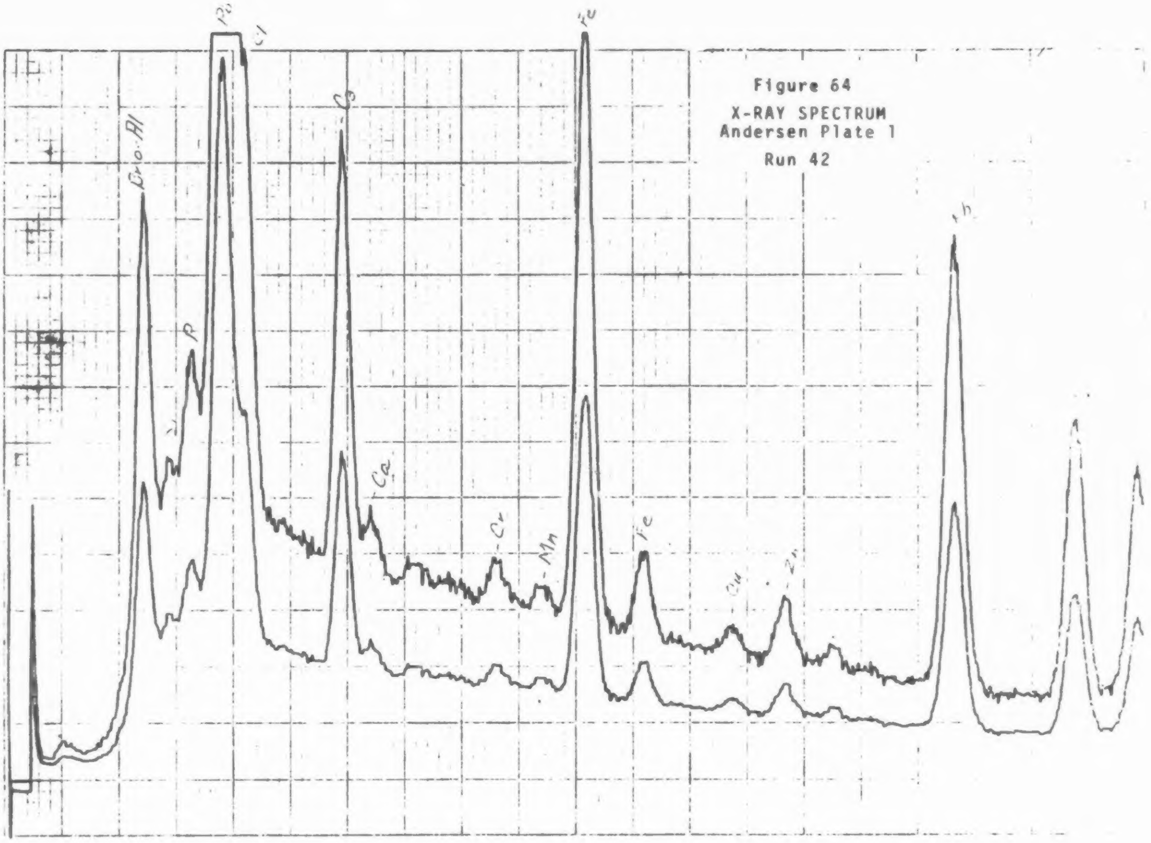


Figure 64
X-RAY SPECTRUM
Andersen Plate 1
Run 42

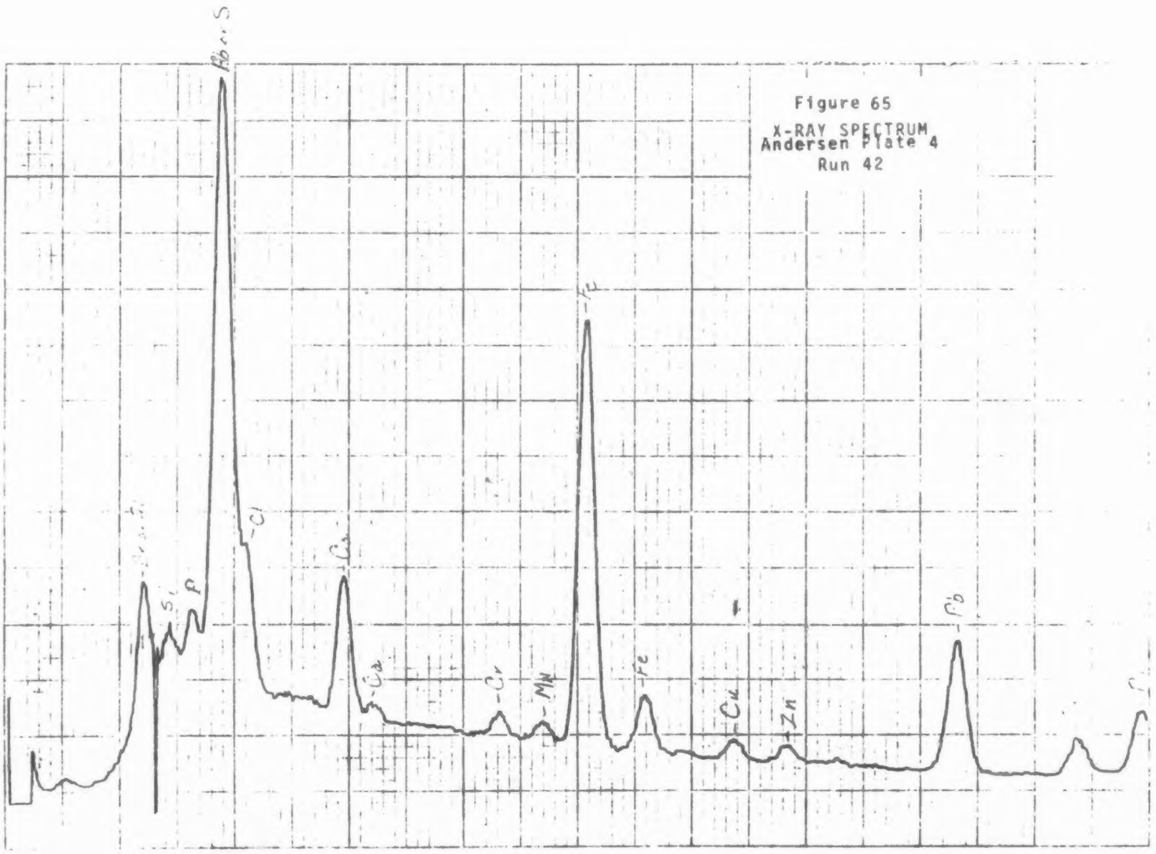


Figure 65
X-RAY SPECTRUM
Andersen Plate 4
Run 42

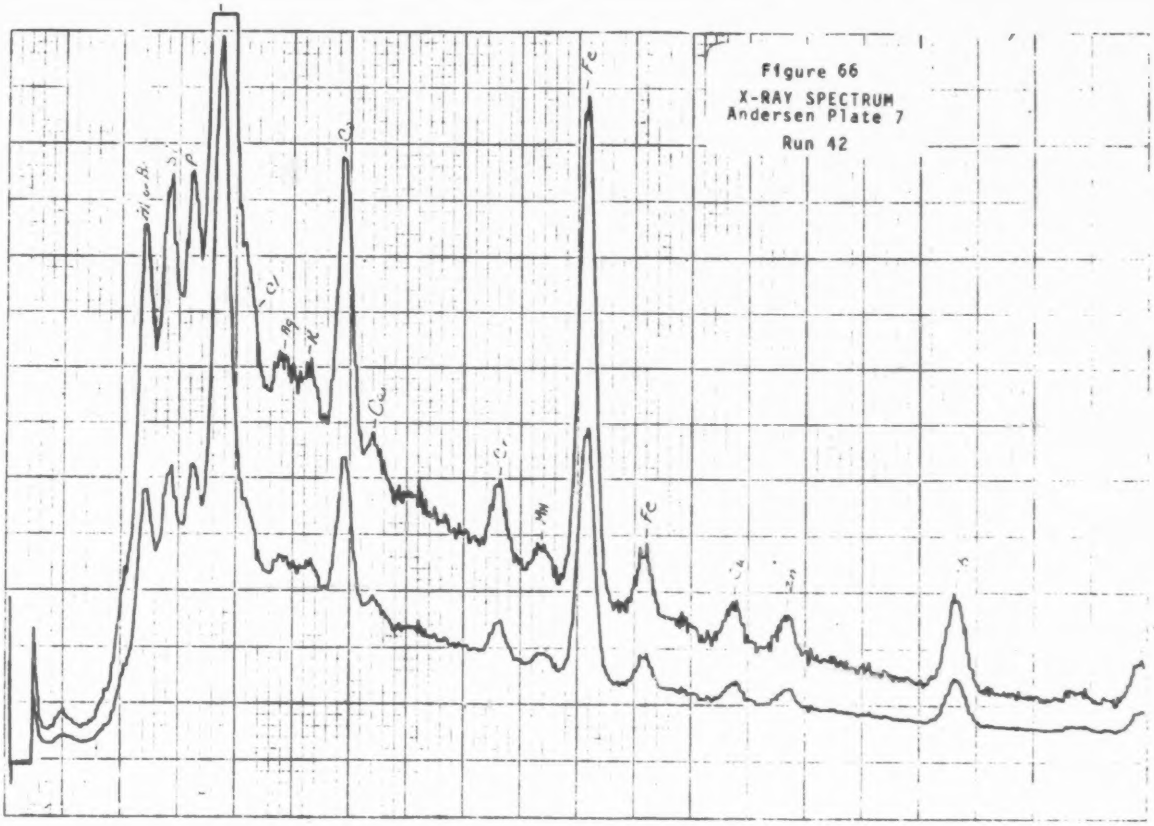


Figure 66

X-RAY SPECTRUM
Andersen Plate 7

Run 42

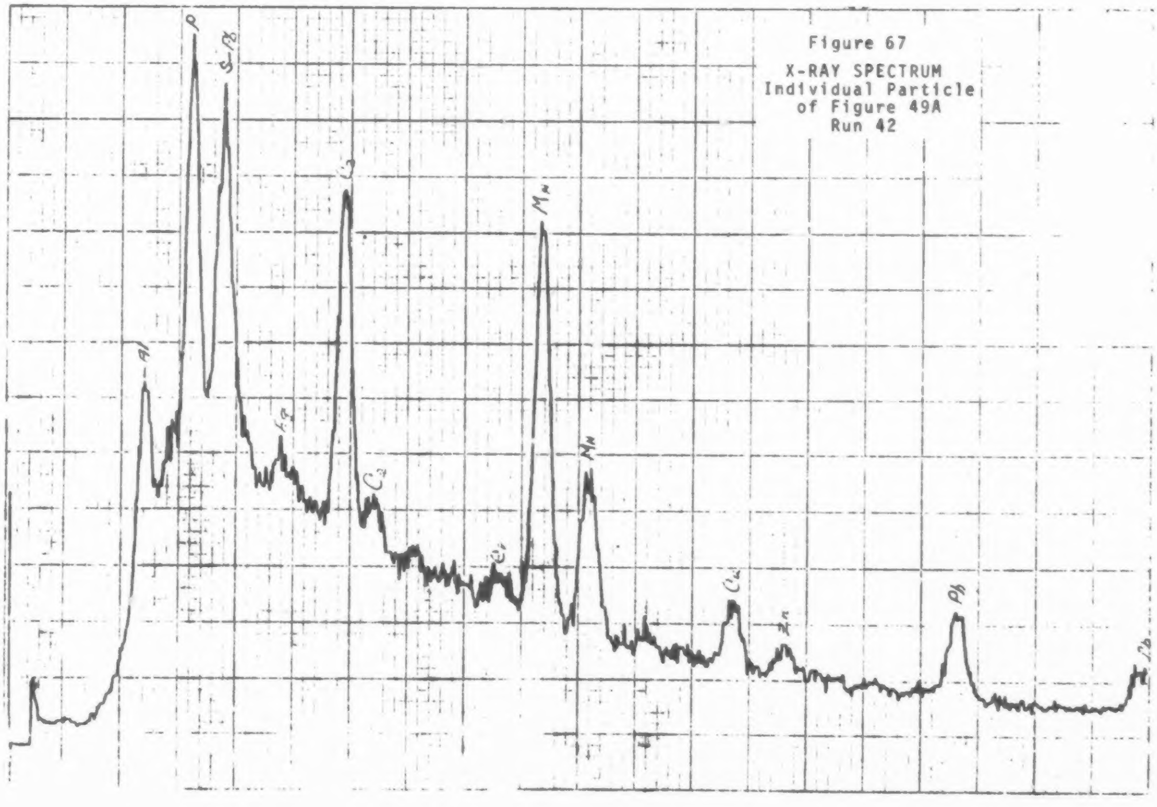


Figure 67

X-RAY SPECTRUM
Individual Particle
of Figure 49A
Run 42

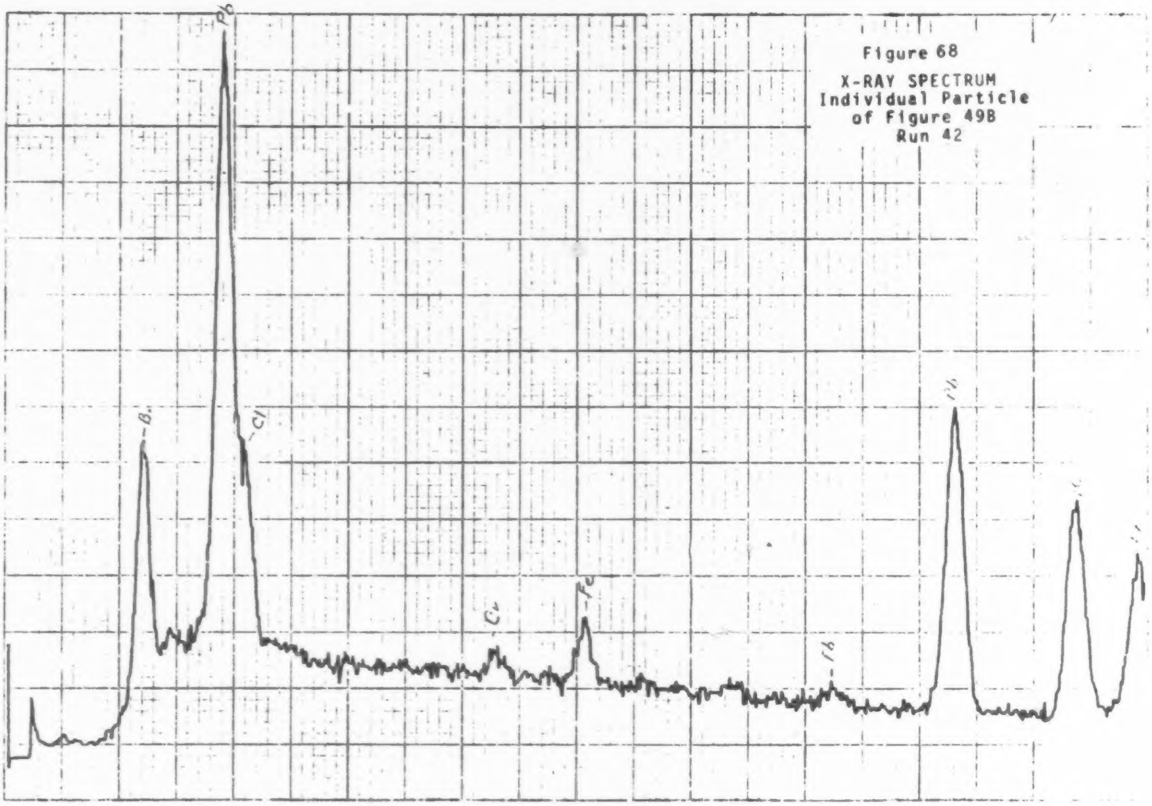


Figure 68

X-RAY SPECTRUM
Individual Particle
of Figure 49B
Run 42

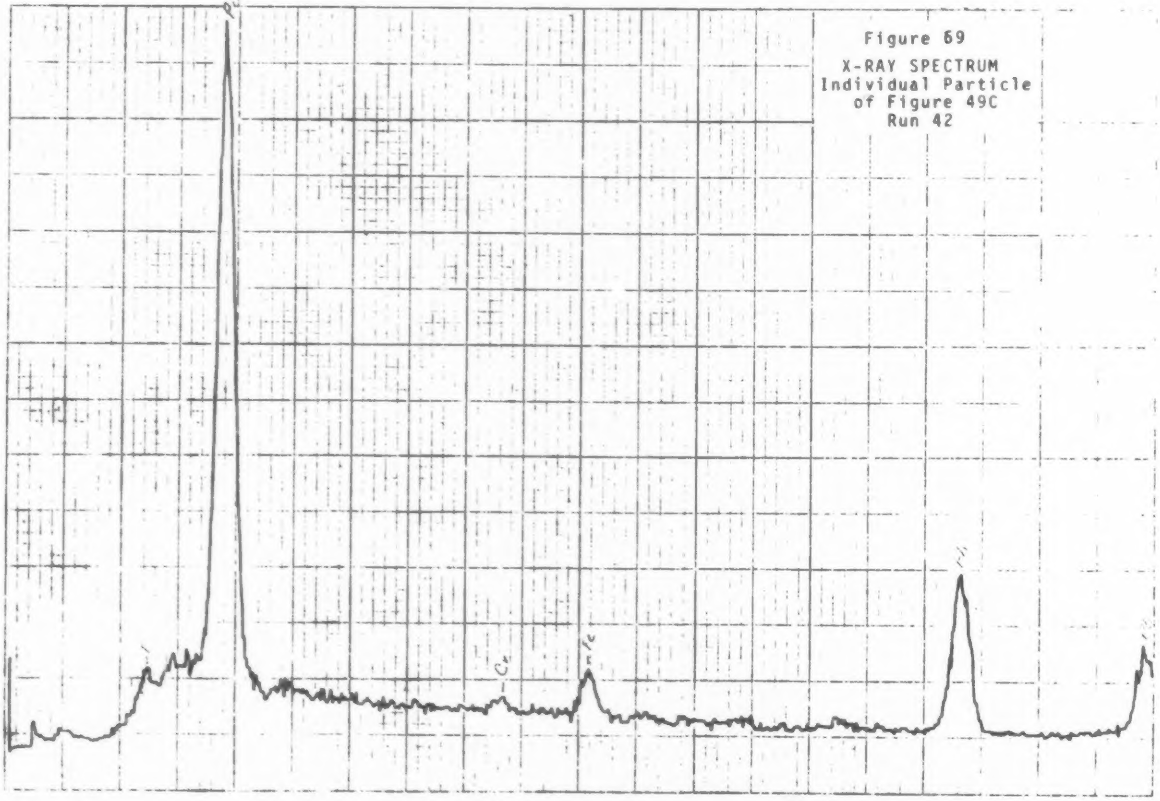


Figure 69

X-RAY SPECTRUM
Individual Particle
of Figure 49C
Run 42

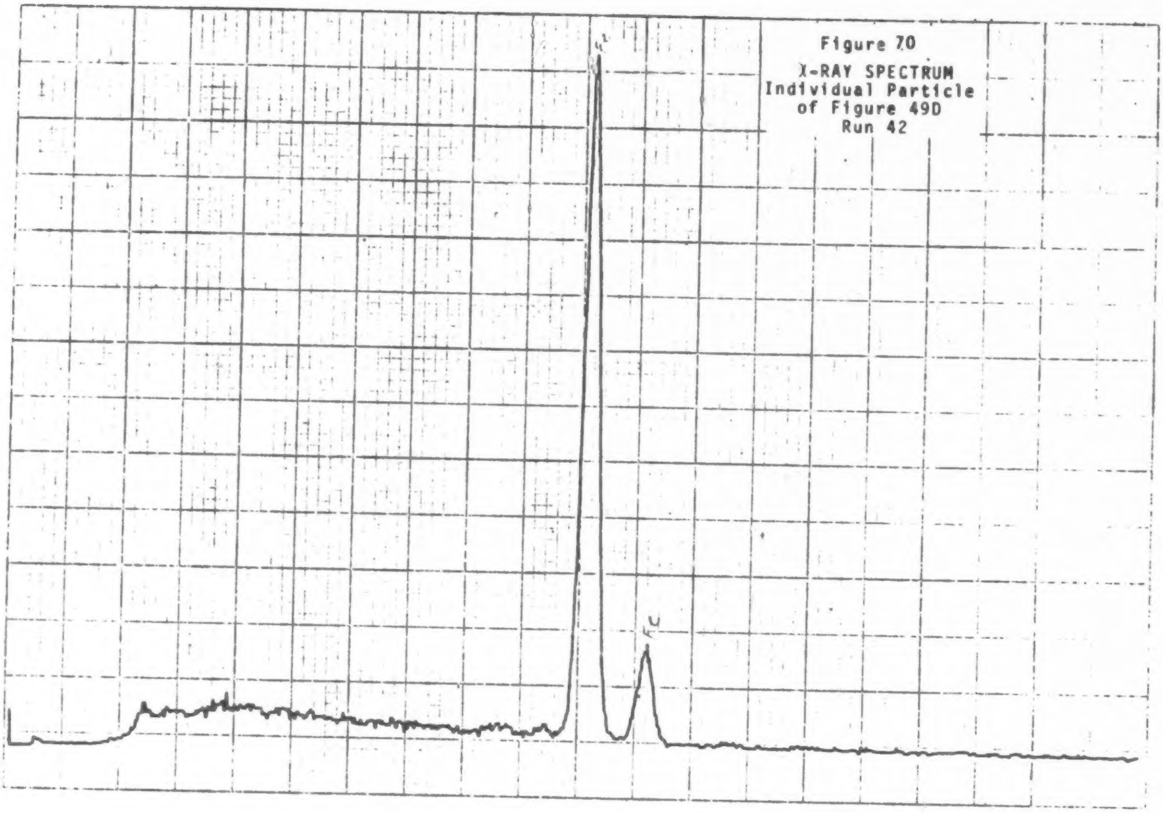


Figure 70

X-RAY SPECTRUM
Individual Particle
of Figure 49D
Run 42

8. Organics

Micro methods have been employed for the determination of benzene solubles, ultraviolet absorptivity, ultraviolet fluorescence, phenolics, and total acidity of exhaust particle size fractions. The details of the procedures have been previously described in the Analytical Methods Section of this report.

In addition, a relative organic concentration has been determined by mass spectrometry, and detailed organic analysis of a single test run exhaust particulate sample was determined utilizing high resolution mass spectrometry.

Table 36 indicates the relative organic content of exhaust particles by size fraction and run number determined by mass spectrometry utilizing methods described earlier.

A hydrocarbon type analysis was made of particulate matter collected in Run 27 by high resolution mass spectrometry using the characteristic hydrocarbon fragment ions for the various types as well as the parent ions for the polyaromatic compounds. This analysis used only the CH ions; no attempt was made to correct this fragment spectrum for those fragments due to the heteratom compounds that were present. The hydrocarbon type analysis is shown in Table 37. The major difference between

TABLE 36

RELATIVE ORGANIC LEVEL BY SIZE FRACTION - MASS SPECTROMETRY METHOD

(Organic Relative Level/mg Sample)

Run No.	Sample Source*	Organic Level (mg)	Sample Wt. (gm)
3	AP-5	3.317	1.15
	6	5.264	0.40
	Filter	1.137	8.70
4	AP-1	0.084	28.20
	2	.109	17.10
	3	.131	11.25
	4	.387	5.00
	5	3.120	4.90
	6	1.654	3.30
	Filter	.877	4.90
	S-1	.020	10.10
	2	.11	10.40
	3	.066	10.25
	4	.093	7.50
	5	.066	9.15
	6	.066	4.70
	7	.060	2.00
5	AP-1	2.565	0.50
	2	1.895	0.50
	5	4.222	0.80
	S-1	0.059	9.45
	2	.11	9.35
	3	.083	10.57
	3'	.10	1.20
	4	.10	10.50
	5	.074	10.50
	6	.086	9.90
	7	.083	10.80
6	AP-1	.200	8.55
	2	.123	6.70
	3	.232	6.30
	4	.668	3.25
	5	2.168	2.65
	6	1.276	10.20
7	AP-1	0.253	12.23
	2	.193	15.85
	3	.193	15.46
	4	.376	8.66
	5	1.389	5.05
	6	1.285	2.61
	Filter	0.628	7.06
8	AP-3	.180	9.70
	4	.426	6.40
	5	1.028	7.80
	6	1.046	9.50
	Filter	0.735	9.90
9	AP-1	.302	9.70
	2	.253	10.30
	3	.225	10.00
	4	.533	7.75
	5	1.671	3.20
	6	2.167	1.60
	Filter	2.527	6.15
11	AP-1	0.187	10.40
	2	.222	8.90
	3	.332	10.20
	4	.547	5.80
	5	1.704	3.30
	6	2.227	4.40
	Filter	1.999	10.90
12	AP-1	0.130	10.61
	2	.144	10.36
	3	.155	9.84
	4	.387	6.45
	5	1.047	6.74
	6	1.440	7.90
	Filter	1.219	6.41
13	AP-1	0.147	10.70
	2	.173	11.30
	3	.290	9.00
	4	.517	6.10
	5	1.646	3.55
	6	1.971	3.55
	Filter	1.700	9.10
14	AP-1	0.115	7.40
	2	.068	9.61
	3	.077	7.66
	4	.127	3.62
	5	.553	3.30
	6	.905	1.90
	Filter	1.034	6.21
16	AP-1	1.955	1.17
	2	1.740	1.17
	3	1.074	0.87
	4	0.655	.50
	5	1.686	.65
	6	2.550	.55
	Filter	0.585	.30
17	AP-1	2.017	1.05
	2	4.053	0.30
	3	1.154	.70
	4	1.250	.65
	5	1.507	.55
	6	2.788	.40
	Filter	0.863	1.20
18	AP-1	.339	12.30
	2	.424	7.74
	3	.636	9.83
	4	.978	9.42
	5	1.785	11.13
	6	2.132	9.24
	Filter	>0.808	13.81
	S-1	.100	11.31
19	AP-1	.171	14.2
	2	.154	19.16
	3	.176	16.15
	4	.312	6.48
	5	.749	4.68
	6	1.148	4.40
	7	1.081	7.95
	Filter	>0.767	4.60
	S-1	.024	8.07
20	AP-1	.093	17.16
	2	.079	17.12
	3	.083	12.02
	4	.196	6.56
	5	.343	5.70
	6	.580	3.58
	7	.669	8.85
	Filter	>.098	0.81
	S-1	.045	11.73
	7	.140	8.95
21	AP-1	.52	3.04
	2	.15	2.31
	3	.14	1.57
	4	.47	1.10
	5	.56	0.71
	6	.84	0.37
	S-1	.55	10.85
	2	.14	9.61
	3	.63	3.08
	4	.55	0.26

*Code: AP- = Andersen Plate-numer
S- = Slit-number

TABLE 36 (Cont.)

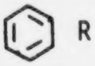
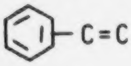
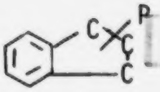
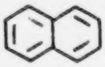
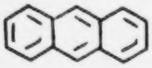
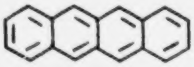
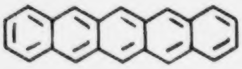
Run No.	Sample Source*	Organic Level (mg)	Sample Wt. (gm)
22	AP-1	1.240	0.705
	2	1.624	.40
	3	1.318	.85
	4	1.538	.70
	5	2.035	1.20
	6	5.049	0.40
	Filter	>1.719	3.65
	S-1	0.095	10.31
	2	.14	10.20
	3	.079	11.73
	4	.088	2.33
23	AP-1	.013	8.3
	2	.016	9.9
	3	.030	7.05
	4	.078	3.00
	5	.413	2.40
	6	.808	1.70
	7	1.051	3.90
	Filter	>1.366	8.30
	S-1	0.055	9.21
	2	.082	11.08
	3	.030	10.76
	4	.079	3.19
	5	.350	0.94
24	AP-1	.015	5.12
	2	.021	4.94
	3	.026	3.80
	4	.16	0.66
	5	.58	.55
	6	1.10	.31
	7	0.95	1.18
	Filter	>.118	8.66
25	AP-1	.030	4.53
	2	.035	5.93
	3	.055	3.74
	4	.140	1.18
	5	.33	0.66
	6	.54	0.70
	7	.61	1.17
	Filter	>.17	9.38
28	AP-1	.036	5.80
	2	.036	6.66
	3	.039	6.40
	4	.18	2.19
	5	.22	1.26
	6	.57	0.31
	Filter	.024	7.42
29	AP-1	.180	0.18
	2	.085	.21
	3	.160	.36
	4	.070	.38
	5	.16	.16
	6	.59	.14
	Filter	>.048	7.31
	Total Hot	.395	11.05
31	AP-1	.196	8.44
	2	.071	4.60
	3	.12	3.32
	4	.22	1.30
	5	.27	1.09
	6	.44	0.4
	Filter	>.354	12.53
	4 cfm	>.31	9.04
33	Filter	.067	9.17
	Filter	.102	9.0
34	AP-1	0.917	9.17
	2	2.140	2.68
	3	0.842	2.55
	4	1.120	2.08
	5	2.071	2.89
	6	4.493	0.98
	7	4.286	4.03
	Filter	1.693	9.46
36	Filter CS	1.326	8.69
	Filter SS	0.038	9.53
38	S-1	.063	15.0
	3	.210	12.75
	5	.750	7.02
	7	.682	1.31
	Filter	.706	2.18
40	AP-1	.148	0.77
	2	.146	2.03
	3	.136	2.28
	4	.250	1.5
	5	.219	1.66
	6	.725	0.24
	Filter	.155	8.38
41	S-1	.213	1.77
	3	.042	6.47
	5	.035	2.01
	Filter	.094	9.9
42	S-1	.079	3.42
	5	.151	2.32
	7	.235	0.35
	Filter	.007	11.0
43	SW-A	.047	4.8
	E	.099	3.1
	F	.020	9.98
	G	.186	0.74
44	AP-1	.585	.21
	2	.702	.23
	3	.904	.37
	4	.464	.36
	5	.645	.54
	6	.479	.33
	7	1.433	.40
	Filter	0.346	7.4
45	AP-1	.525	0.15
	2	3.04	.04
	3	3.855	.03
	4	2.06	.07
	5	2.35	.05
	6	0.589	.21
	7	.609	.21
	Filter	.067	11.02
46	AP-1	1.06	0.26
	2	1.145	.18
	4	0.989	.16
	5	.987	.26
	6	1.138	.18
48	AP-1	3.14	.20
	2	0.759	.20
	3	1.42	.10
	4	1.175	.11
	5	0.888	.19
	6	1.429	.12
53	AP-1	0.51	.20
	2	1.16	.10
	3	1.08	.10
	4	0.74	.15
	5	.63	.20
	6	4.48	.20

*Code:
AP- = Andersen Plate-number
S- = Slit-number
SW- = Sweepings-letter

the two samples, A and B, is the greater abundance of aromatics in Sample A and, although not evident from this table, the presence of what appears to be more lubricating oil in Sample B than in Sample A. Sample A contains a large amount of the C_nH_{2n-8} type of which most is C_8H_8.

TABLE 37

HYDROCARBON CHAIN TYPE ANALYSIS
HIGH RESOLUTION MASS SPECTROMETRY

Hydrocarbon Type	Sample A* 7 mg 10% Organic	Sample B 122 mg <1.0% Organic	Possible Structures
	Volume %		
$C_nH_{2n} + 2$	21.0	46.0	
C_nH_{2n}	23	20	
$C_nH_{2n} - 2$	14	14	
$C_nH_{2n} - 4$	3	3	
$C_nH_{2n} - 6$	26	16	
$C_nH_{2n} - 8$	10	<0.1	 
$C_nH_{2n} - 10$	1	0.1	
$C_nH_{2n} - 12$	0.8	0.63	
$C_nH_{2n} - 14$	0.02	0.15	
$C_nH_{2n} - 16$	0.83	--	
$C_nH_{2n} - 18$	0.45	0.35	
$C_nH_{2n} - 20$	0.05	--	
$C_nH_{2n} - 22$	--	0.09	
$C_nH_{2n} - 24$	--	0.14	
$C_nH_{2n} - 26$	--	--	
$C_nH_{2n} - 28$	--	--	
$C_nH_{2n} - 30$	0.48	--	

*Sample A - 7.20 mg, 10% organic, from Andersen plates 3, 4, 5, 6 from three different Andersen samplers from the same run.

Sample B 122.25 mg <1% organic sweepings from dilution tube.

CHO Types - Both samples contain aromatic oxygenated compounds of the $C_nH_{2n-6}O$ type and what can be unsaturated ketones and/or aldehydes through C_7.

CHO_2 Types - Both samples contain the aromatic oxygenated compounds of the $C_nH_{2n-6}O_2$ type. The most abundant materials are what are probably large aliphatic acids. Sample A has only the C_{14} acid while Sample B has the C_{14}, C_{16}, and C_{18} acids.

CHN Types - The most abundant types present in both samples are the $C_nH_{2n-5}N$ types where n is equal to 5 through 7.

CHN_2 Types - These types are low concentration as shown in Table 37. Aromatic types are the most predominant.

Shown in Table 38 is the percentage of the most abundant ion types for samples from the dilution tube and Andersen sampler for Run 27 (Fuel Type A). Data obtained via high resolution mass spectrometry utilizing direct introduction probe and data reduction using the Shell Oil HIRES programs. Only the elements listed were considered and these combinations accounted for about 85-90 percent of the ion observed. Volatile lead compounds, other chlorinated and brominated compounds are not included.

TABLE 38

PERCENT OF TOTAL ION CONTENT VIA
HIGH RESOLUTION MASS SPECTROMETRY

Ion Types	Sample A	Sample B	Hexanol-1	3-Octanone	2-Ethylhexyl Acetate
CH's	90.2	89.3	92	47	73
CHO's	4.2	3.2	8	53	19
CHO_2's	4.3	6.8	-	-	8
CHN's	1.3	0.7	-	-	-
CHN_2's	0.03	0.01	-	-	-

Sample A - 7.20 mg, 10% organic, Andersen Plates 3, 4, 5, 6; taken from three different Andersen samplers from the same run.

Sample B - 122.25 mg, <1% organic, dilution tube sweeping sample.

The table also indicates the percent of ion types for an alcohol, a ketone, and an ester so that a comparison may be made with the sample values. It is evident that although the heteratom types are present, the bulk of each sample is hydrocarbon.

A portable cycloidal mass spectrometer was used to monitor the hot engine exhaust at the manifold and in the tailpipe just past the muffler during Run 16 while in the conditioning sequence. Results are shown as mass spectra in Figures 71-78.

Table 39 reflects data on the organic content of collected exhaust particles by run number and source. The weight percent solubility in benzene/methanol and the relative ultraviolet absorbance value are further measures of total organic content of the collected exhaust particulate. Table 40 shows only the UV absorbance of Runs 3-17, whereas Table 41 shows the UV fluorescence levels. Table 42 provides data on the further analysis of the benzene soluble fraction of collected exhaust particulate. The analytical procedures used are presented in the Experimental Procedures Section.

Analysis of benzene extracts of collected exhaust particles for various carbonyls via polarographic techniques is shown in Table 43. Values shown are corrected for solvents and reagents used during determinations.

Further analysis of benzene soluble fractions by Pulse Polarography is shown in Table 44. See the Experimental Procedures Section for method.

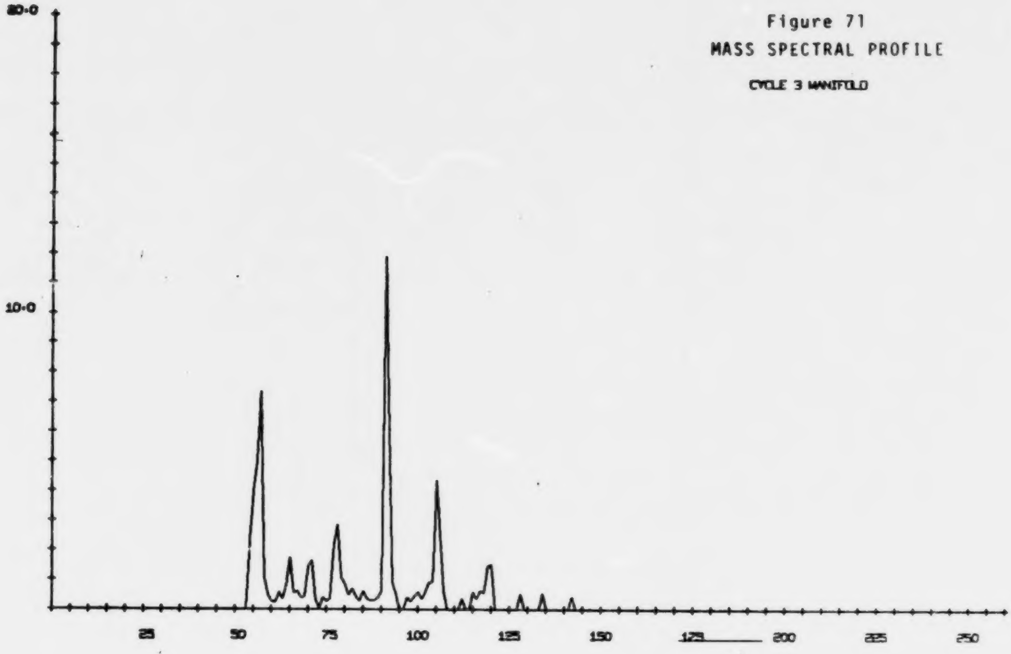


Figure 71
MASS SPECTRAL PROFILE

CYCLE 3 MANIFOLD

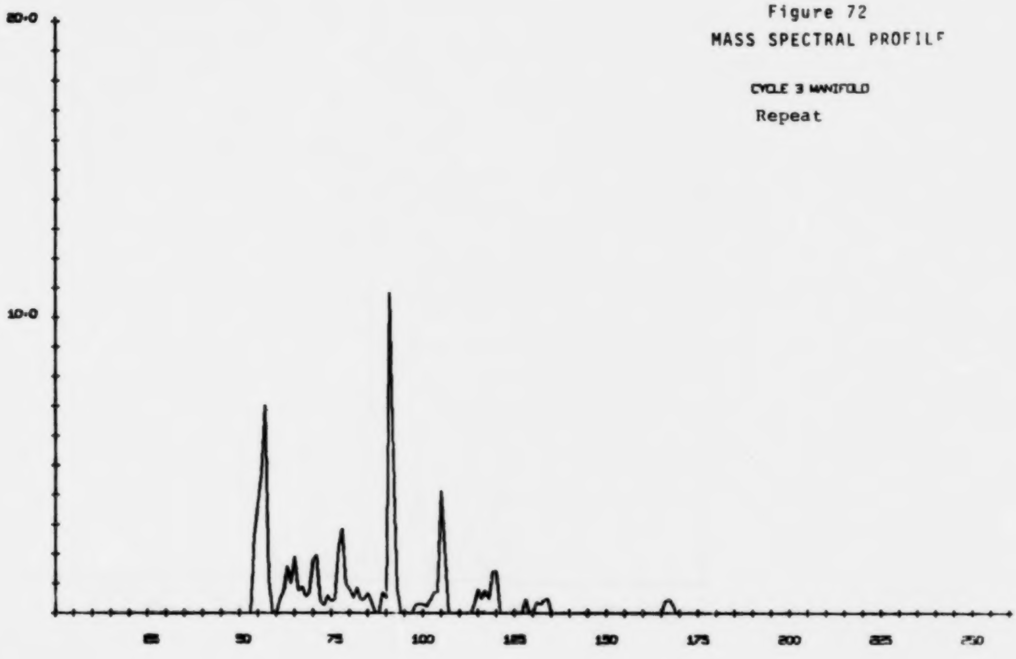


Figure 72
MASS SPECTRAL PROFILE

CYCLE 3 MANIFOLD
Repeat

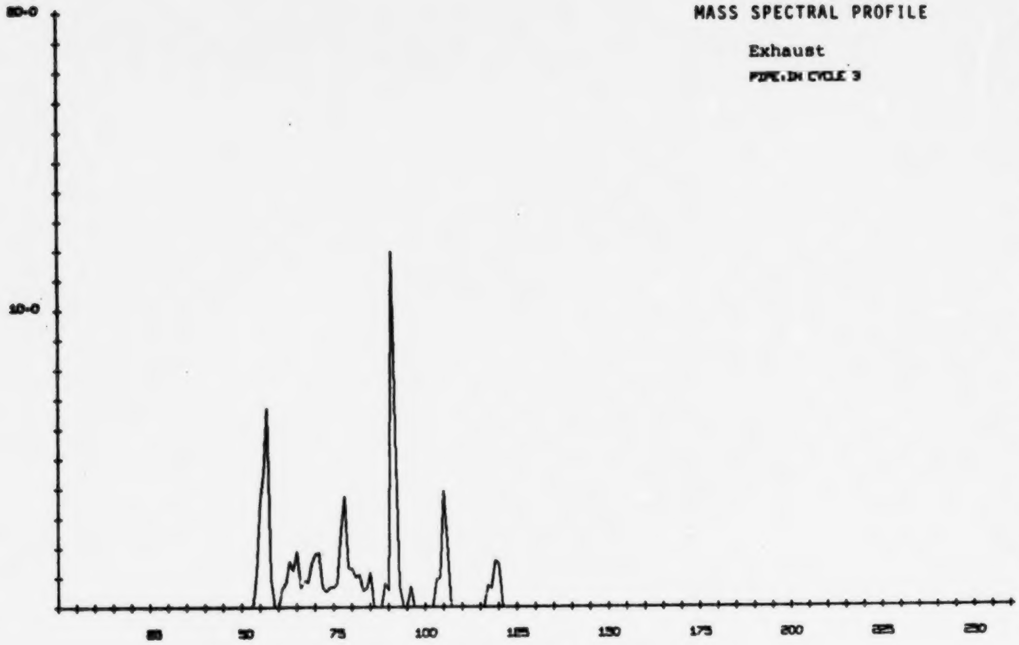


Figure 73
MASS SPECTRAL PROFILE
Exhaust
PIPE:IN CYCLE 3

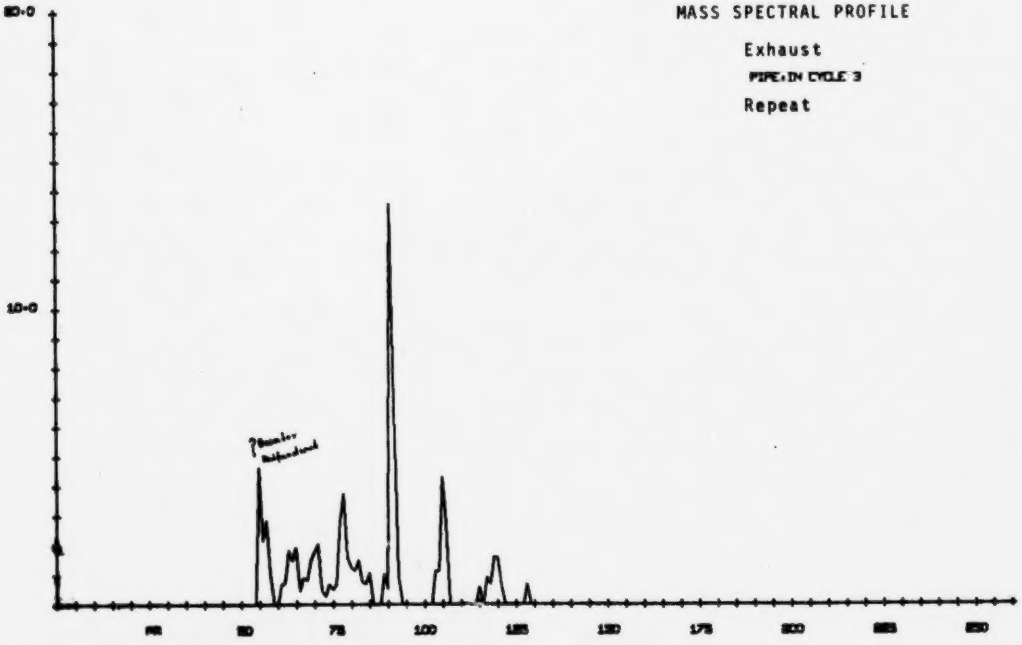


Figure 74
MASS SPECTRAL PROFILE
Exhaust
PIPE:IN CYCLE 3
Repeat

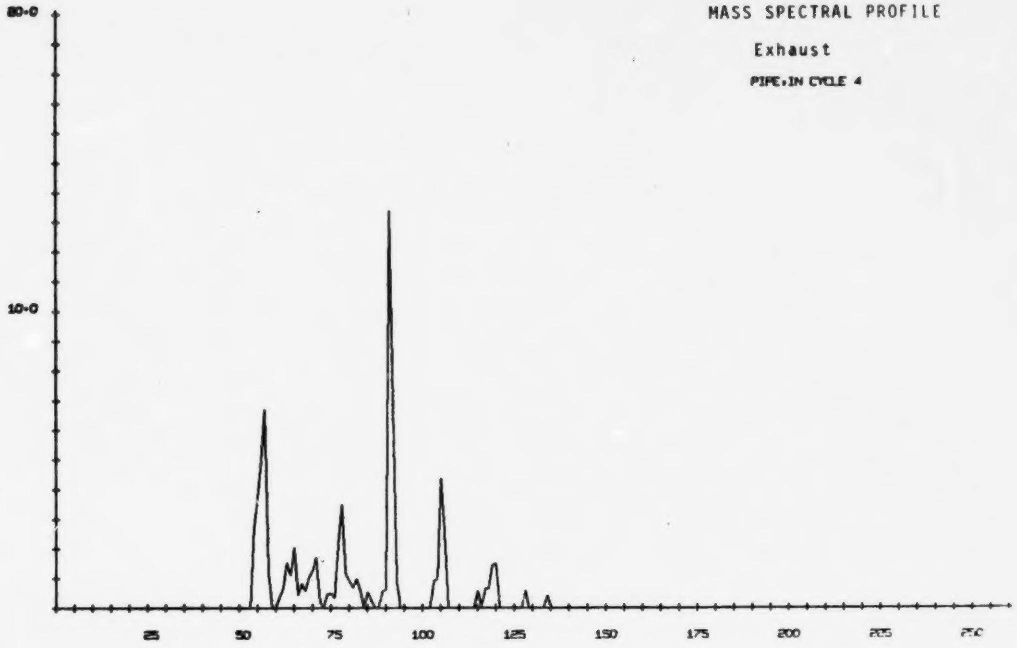


Figure 75
MASS SPECTRAL PROFILE
Exhaust
PIPE,IN CYCLE 4

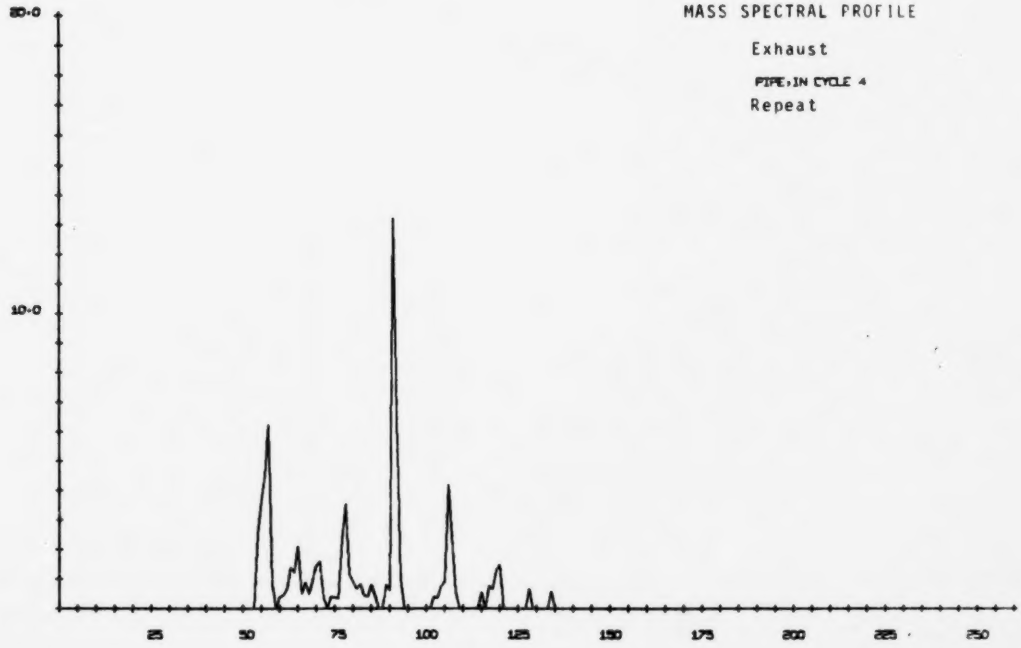


Figure 76
MASS SPECTRAL PROFILE
Exhaust
PIPE,IN CYCLE 4
Repeat

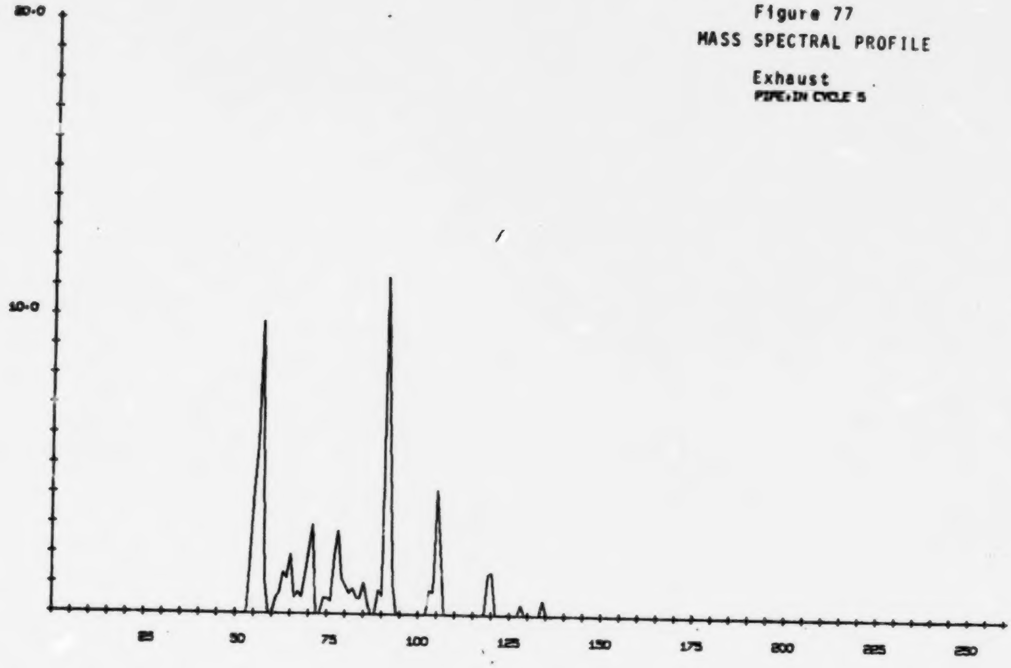


Figure 77
MASS SPECTRAL PROFILE

Exhaust
PIPE:IN CYCLE 5

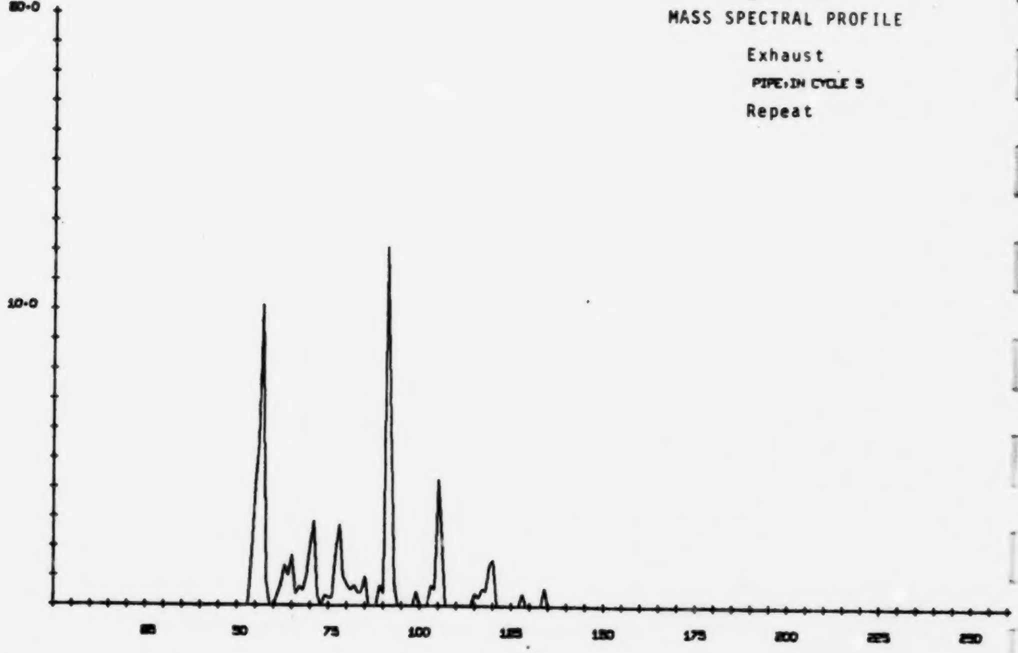


Figure 78
MASS SPECTRAL PROFILE

Exhaust
PIPE:IN CYCLE 5
Repeat

TABLE 39

ORGANIC ANALYSIS OF COLLECTED EXHAUST PARTICULATES BY RUN NUMBER

Run No.	Sample Source	Amount Collected (mg)	Benzene and Methanol Soluble (wt. %)[f]	Acidity Calc. as ϕCO_2H (%)	Phenolics Calc. as ϕOH (%)	Rel. UV Value (per mg)
19	1 cfm Millipore filter	164.7	5.4	0.29	0.08	2880
	1 cfm Glass fiber filter	18.9	8.6	.68	.08	3500
20	1 cfm Glass fiber filter	21.1	7.8	.23	.06	3290
	1 cfm Millipore filter	153.5	5.6	.41	.21	3000
21	1 cfm Millipore filter	39.2	38.3	7.8	1.8	20,800
22	1 cfm Glass fiber filter	27.1	54.6	0.34	0.21	9410
	1 cfm Glass fiber filter	30.2	50.5	.83	.31	8140
23	1 cfm Glass fiber filter	149.0	7.8	.34	.10	2720
	Andersen Plates 1,2,3	70.9	0.8	.04	.02	279
	Andersen Plates 4,5,6	20.9	4.7	.38	.12	1970
24	4 cfm Glass fiber filter	159.2	1.7	.11	.02	500
	4 cfm Glass fiber filter	161.7	1.9	k	.01	550
25	4 cfm Glass fiber filter	139.5	2.5	.23	.03	630
	4 cfm Glass fiber filter	118.8	2.3	.14	.03	610
28	4 cfm Glass fiber filter	171.0	3.6[h]	.35	.04	710
29	1 cfm Glass fiber filter	12.0	6.7[h]	1.6	.02	1700
	Total exhaust hot filter	31.1	16.6[h]	g	g	190
	Andersen Plates 1,2,3,4	4.4	70.0[h]	Not calc.	Not calc.	5050
	Andersen Plates 5,6,7	1.7	35.0[h]	Not calc.	Not calc.	1350
30	4 cfm Glass fiber filter (Steady State)	116.0	3.7	0.38	0.03	1210 ±40
	1 cfm Glass fiber filter (Steady State)	31.6	6.0	.44	.04	1290
	4 cfm Glass fiber filter (FTP-Cy)	13.3	(<1.5)[k]	.68	k	1020
	1 cfm Glass fiber filter (FTP-Cy)	5.1	k	<1.5	k	960
31	1 cfm Glass fiber filter	127.3	5.1	0.54	0.08	1230
	4 cfm Glass fiber filter	735.6	2.6	.09	.05	380
	Andersen Plates 1,2,3,4	24.4	2.7	.62	k	310
	Andersen Plates 5,6,7	12.8	3.3	.70	k	1080
	Total exhaust hot filter	462.7	(<0.5)[k]	g	g	15[k]
34	4 cfm Glass fiber filter	196.2	20.9	0.40 ± 0.05	0.07	4420
40	4 cfm Glass fiber filter	145.5	6.4[h]	0.80 ± 0.05	.20	1990
43	1 cfm Millipore filter	6.5	<6[k]	4.5	1.1	6450
44	4 cfm Glass fiber filter	156.4	2.4	1.0	.44	3040
45	1 cfm Millipore filter	12.6	k	1.3	.41	3450
53	4 cfm Glass fiber filter	4.3	5.6	k	<.07[k]	1140
	4 cfm Glass Fiber filter	6.8	13.4	0.53	<.11[k]	3590

ⓕ Corrected by subtraction of blank

ⓖ Not considered

ⓗ Value for benzene soluble material

ⓚ Value for blank greater or same magnitude as sample; calculation not meaningful.

TABLE 40

RELATIVE AMOUNTS OF UV ABSORBING MATERIAL PRESENT ON ANDERSEN PLATES

Run #	Plate #2		Plate #4		Plate #5	
	mg sample	Absorbance*	mg sample	Absorbance*	mg sample	Absorbance*
3	7.93	240	2.19	750	1.40	2020
4	24.6	520	13.7	850	6.15	4620
4	10.8	560	6.27	680	3.54	1550
5	0.13	810	0.18	360		
6	8.56	680	2.71	2620	3.92	2940
7	15.3	720	8.73	830		
8	22.7	380	8.27	1000		
9	15.4	730	7.86	1810	4.93	4460
11	24.1	640	6.34	1780	5.39	4220
12	19.7	370	8.55	860	7.32	2360
13	14.9	500	5.34	1950	3.38	3440
14	8.49	300	4.44	480	2.65	1160
15 Blank	0.1	2400			<0.1	assuming 0.1 mg 13400
16	1.1	13500	0.3	34400	0.6	17500
17	0.9	8670	0.6	10700	1.0	6940

---

*Values are calculated on a basis of Absorbance @255mμ for 1.0 mg of sample in 1.0 ml of solvent x 1000. A relative value for the total amount UV absorbing material on a particular plate can be obtained by multiplying the sample weight in mg times the above value.

mg sample = Sample weight in milligrams

TABLE 40A

RELATIVE AMOUNTS OF UV ABSORBING AND FLUORESCENT MATERIALS PRESENT IN SWEEPING AND SLIT SAMPLES

(See Notes at Bottom of Tables

Run #		Sample Wt. in mg	Relative Absorbance Values	Relative Fluorescent Values
13 - Sweeping	A	9.49	340	320
	B	9.41	180	110
	C	9.31	180	110
	D	8.95	600	300
	E	8.85	800	350
	F	7.69	910	340
	G	12.1	770	290
Slit	1	11.1	40	20
	2	7.90	50	30
	3	9.49	20	20
14 - Sweeping	A	13.4	210	160
	B	9.83	90	50
	C	11.9	40	30
	D	8.70	270	140
	E	4.48	1010	510
Slit	1	8.87	50	30
	2	10.0	30	10

TABLE 41

RELATIVE AMOUNTS OF FLUORESCENT MATERIAL PRESENT ON ANDERSEN PLATES

Run #	Plate #2		Plate #4		Plate #5	
	mg sample	Fluorescence*	mg sample	Fluorescence*	mg sample	Fluorescence*
3	7.93	240	2.19	570	1.40	1580
4	24.6	190	13.7	440	6.15	1790
4	10.8	240	6.27	350	3.54	880
5	0.13	840	0.18	500		
6	8.56	260	2.71	1320	3.92	1750
7	15.3	310	8.73	470		
8	22.7	130	8.27	420		
9	15.4	140	7.86	280	4.93	320
11	24.1	60	6.34	250	5.39	190
12	19.7	70	8.55	180	7.32	190
13	14.9	110	5.34	320	3.38	550
14	8.49	100	4.44	230	2.65	180
15 Blank	0.1	650			<0.1	assuming 0.1 mg 5400
16	1.1	290	0.3	3570	0.6	2260
17	0.9	1480	0.6	2380	1.0	1480

---

*Values are calculated on the basis of area (in.^{2} x 100, with a planimeter) for 1.0 mg of sample in 1.0 ml of solvent, with instrument settings of excitation wavelength = 290mμ, slits = 2mm, sensitivity = 0.01, and vertical scale of recorder at a setting of 5. A relative value for the total amount of fluorescent material on a particular plate can be obtained by multiplying the sample weight in mg times the above value.

TABLE 42

ANALYSIS OF BENZENE SOLUBLE FRACTION OF COLLECTED EXHAUST PARTICULATES BY RUN NUMBER

Run No.	Sample Source	Benzene Soluble**		Absorptivity (255 nm)	Acidity Calc. as ØCO$_2$H (%)	Phenolics Calc. as ØOH (%)	Ratios of Chromogenics to Phenolics		
		Soluble Methanol (%)	Insoluble Methanol (%)				330 nm	420 nm	450 nm
19	1 cfm Millipore filter	5.4	1.5	53	5.3	1.6 ± 0.2	-	0.7	-
	1 cfm Glass fiber filter	8.6	0.0	41	7.9	0.9 ± 0.5	-	.6	-
20	1 cfm Glass fiber filter	7.8	0.3	38	3.0	0.7 ± 0.5	-	.8	-
	1 cfm Millipore filter	5.6	.8	54	7.3	3.7 ± 0.4	-	-	0.4[n]
21	1 cfm Millipore filter	38.3[m]	.8	54	~20	4.6	1.1	0.3	-
22	1 cfm Glass fiber filter	54.2	13.9	17	1.6	0.4 ± 0.1	0.7	-	-
	1 cfm Glass fiber filter	50.6	9.6	16	0.7	0.6 ± 0.1	0.4	0.4	-
23	1 cfm Glass fiber filter	7.8	3.3	35	4.4	1.3 ± 0.1	0.6	0.5	0.5
	Andersen Plates 1,2,3	0.8	0.0	35	5.3	2.8	-	-	0.5
	Andersen Plates 4,5,6	4.7	1.3	42	8.1	2.5	-	-	0.4[n]
24	4 cfm Glass fiber filter	1.7	0.2	29	6.7	0.9 ± 0.1	0.8	0.7	-
	4 cfm Glass fiber filter	1.9	0.3	29	k	0.6 ± 0.1	0.9	0.7	-
25	4 cfm Glass fiber filter	2.5	0.3	26	9.9	1.2 ± 0.1	0.8	0.4	0.3
	4 cfm Glass fiber filter	2.3	0.3	27	6.8	1.2 ± 0.1	0.6	0.4	0.3
28	4 cfm Glass fiber filter	3.6[h]	g	21	9.8	1.1 ± 0.2	-	0.6	0.6
29	1 cfm Glass fiber filter	6.7[h]	g	29	23.8	1.5 ± 1.1	-	1.2	-
	Total exhaust hot filter	16.6[h]	g	1.2	g	g	g	g	g
	Andersen Plates 1,2,3,4	70.0[h]	g	7.2	k	k	-	-	-
	Andersen Plates 5,6,7	35.0[h]	g	3.9	k	k	-	-	-
30	4 cfm Glass fiber filter (Steady State)	3.7[h]	g	34	10.2	0.8 ± 0.3	-	0.8	0.7
	1 cfm Glass fiber filter (Steady State)	6.0[h]	g	23	7.4	0.7 ± 0.7	-	0.5[n]	-
	4 cfm Glass fiber filter (FTP-Cy)*	(<1.5)[k]	g	k	k	k	-	0.2	-
	1 cfm Glass fiber filter (FTP-Cy)	k	g	k	(<14)[k]	k	-	0.8	-
31	1 cfm Glass fiber filter	5.1[h]	g	25	10.6	1.6 ± 0.2	-	2.4	-
	4 cfm Glass fiber filter	[illegible].6[h]	g	15	3.8[m]	2.0 ± 0.1	-	0.7	-
	Andersen Plates 1,2,3,4	2.7[h]	g	12	23.2[m]	k	-	-	-
	Andersen Plates 5,6,7	3.3[h]	g	33	21.0[m]	k	-	-	-
	Total exhaust hot filter	(<0.5)[k]	g	k	g	g	g	g	g
34	4 cfm Glass fiber filter	20.9	8.4[q]	21	2.0 ± 0.3	0.35	-	0.3	0.4
40	4 cfm Glass fiber filter	6.4	0.0	31	12.4 ± 0.9	3.1 ± 0.1	0.7	1.1	-
43	1 cfm Millipore filter	<6	0.0	k	k	k	1.4	0.5	-
44	4 cfm Glass fiber filter	2.4	0.1	124	41.9	17.3	-	1.5	-
45	1 cfm Millipore	k	0.0	k	k	k	2.1	0.8	-
53	4 cfm Glass fiber filter	5.6	40.0	20	k	<1.2[k]	1.0	-	-
	4 cfm Glass fiber filter	13.4	1.5	27	4.0	<0.8[k]	1.1	0.4	0.5

*FTP-Cy = California 7 mode cycle **See Procedure on page 63

ⓖ Not considered

ⓗ Value for benzene soluble material

ⓚ Value for blank greater or same magnitude as sample; calculation not meaningful

ⓜ Accuracy may be poor because of large blank correction

ⓝ Broad absorbance peak

ⓠ Insolubles consisted of a black tar and a viscous liquid having the IR characterization of aliphatic hydrocarbon (i.e. absorbance peaks at 2900, 1460, 1370, and 750 cm^{-1}.

TABLE 43

BENZENE EXTRACTS OF EXHAUST PARTICULATES - POLAROGRAPHIC METHOD
(Values in Micrograms/ml)

Run No.	Source	HCHO	CH_3CHO	ØCHO	$Ø_2CO$
19	Filter 1/2 cfm	*	<5	<6	*
19	" 1 cfm	<1	<2	<3	14
20	" 1/2 cfm	0.4	<2	<3	8.3
20	" 1 cfm	<2	<2	*	16
21	" 1 cfm	<5	17	<6	29.0
22	" 1 cfm	1.0	<2	<6	17
22	" 1 cfm	*	*	*	31
Blanks	Solvent Blank	<1	<2	<3	22
	Glass Filter	<2	<5	<6	22
	Membrane Filter	<2	<5	<6	20
23A	Andersen 1,2,3	<2	*	<6	*
23B	Andersen 4,5,6	*	<5	<6	*
23	Filter 1 cfm	<1	<2	<3	<20
24	" 4 cfm	13	<10	<6	13
**25	" 4 cfm	<2	<5	<6	<20
**25	" 4 cfm	<1	<5	*	<20
28	" 4 cfm	5.6	4.0	<6	17
29	Andersen 1,2,3,4	<1	1.5	<3	19
29	Andersen 5,6,7	<1	2.4	<3	7.4
30	Filter 4 cfm	11	<10	<10	44
30	" 1 cfm	5.4	2.5	<6	16
30	" 4 cfm	<4	*	<6	12
30	" 1 cfm	2.1	<5	<6	27
31	" 1 cfm	9.5	<5	6.5	32
31	" (4) 4 cfm	4.3	<5	4.8	11
40	" 4 cfm	1.7	<2	3.7	17
44	" 4 cfm	1.5	<5	4.2	<20
45	" 1 cfm	1.8	9.2	<6	<20
53	" 4 cfm	<2	<5	<6	55
53	" 4 cfm	1.6	<5	<6	24

*Interference prevents determination.

**Run 25 two 4-cfm filters were used on the same run and same sample probe.

TABLE 44
ANALYSIS OF PARTICULATE BENZENE SOLUBLES VIA PULSE POLAROGRAPHY FOR SELECTED TEST RUNS

Run No.	Sample Source	Particulate Analyzed (mg)	Benzene and Methanol Soluble Residue (mg)[f]	Vol. (ml)	µg/ml (Gross)			% in Soluble Residue	
					Pb	Aromatic Ketone as $(C_6H_5)_2CO$	RCHO	Pb	Total Carbonyl Calc. as $(C_6H_5)_2CO$[h]
19	1 cfm Millipore filter	75.7	4.08	5	31	14	ND[g]	3.8	<1.7
	1 cfm Glass fiber filter	18.9	1.63	5	17	i	ND	5.2	i
20	1 cfm Glass fiber filter	21.1	1.65	5	ND	16	ND	<1.8	<4.8
	1 cfm Millipore filter	36.9	2.06	5	ND	8.3	ND	<1.5	<2.0
21	1 cfm Millipore filter	39.2	n	5	48	29	17 as CH_3CHO	m	m
22	1 cfm Glass fiber filter	27.1	14.65	10	13	17	1 as H_2O	0.9	<1.1
	1 cfm Glass fiber filter	30.2	15.26	10	ND	31	i	<0.4	0.6 to 2.0
23	1 cfm Glass fiber filter	149.0	11.56	10	37	ND	ND	3.2	<1.7
	Andersen Plates 1,2,3	57.0	0.45	5	ND	i	ND	m	m
	Andersen Plates 4,5,6	18.7	0.88	5	22	i	ND	m	m
24	4 cfm Glass fiber filter	159.2	2.55	5	19	13	1.3 as H_2CO	3.7	<2.5
25	4 cfm Glass fiber filter	139.5	3.20	4	27	ND	ND	3.4	<2.5
	4 cfm Glass fiber filter	118.8	2.49	4	ND	ND	ND	<1.9	<3.2
28	4 cfm Glass fiber filter	171.0	6.1	5	20	17	5.6 as H_2CO 4.0 as CH_3CHO	1.6	0.8 to 2.5
29	Andersen Plates 1,2,3,4	4.4	0.49	5	ND	19	1.5 as CH_3CHO	m	m
	Andersen Plates 5,6,7	1.7	0.07	5	ND	7.4	2.4 as CH_3CHO	m	m
30	4 cfm Glass fiber filter	116.0	4.3	5	38	44	11 as H_2CO	4.4	2.5 to 5.1
	1 cfm Glass fiber filter (Steady-State)	31.[illegible]	1.9	5	10	16	5.4 as H_2CO	2.6	<4.2
	4 cfm Glass fiber filter (FTP-Cy)	13.3	n	5	ND	12	ND	m,n	m,n
	4 cfm Glass fiber filter (FTP-Cy)	5.1	n	5	8	27	2.1 as H_2CO	m,n	m,n
31	1 cfm Glass fiber filter	127.3	6.5	5	640[q]	32	9.5 as H_2CO 6.5 as C_6H_5CHO	49.2[q]	1.6 to 3.3
	4 cfm Glass fiber filter	735.6	18.2	10	82	11	4.3 as H_2CO 4.8 as C_6H_5CHO	4.5	<1.0
40	4 cfm Glass fiber filter	145.5	9.32	10	130[r]	17	1.7 as H_2CO 3.7 as C_6H_5CHO	13.9[r]	<2.5
44	4 cfm Glass fiber filter	156.4	3.82	5	430[t]	ND	1.5 as H_2CO 4.2 as C_6H_5CHO	56.3[t]	<2.6
45	1 cfm Millipore filter	12.6	n	5	i	ND	1.8 as H_2CO 9.2 as CH_3CHO	m	m
53	4 cfm Glass fiber filter	4.3	0.24	5	ND	24	1.6 as H_2CO	m	m
	4 cfm Glass fiber filter	6.8	0.91	5	ND	55	ND	m	m
-	Benzene solvent	-	0.05	5	ND	12 to 23	ND	m	m
Glass filter blank		-	0.4 0.2	5	ND	4 to 22	ND	m	m
Millipore filter blank		-	30.0 2	5	i	ND	ND	m	m

ⓕ Net after subtraction of blank residue weight.

ⓖ Not detected. For 2-ml aliquots the detection limits are 2 µg/ml for H_2CO; 5 µg/ml for RCHO calc. as CH_3CHO; 6 µg/ml for ArCHO calc. as C_6H_5CHO; 6 µg/ml for Pb.

ⓗ When value of µg/ml is less than the blank value, the calculated, uncorrected value is expressed as "less than." Gelman glass filters and solvent gave blanks of 22 µg/ml calc. as $(C_6H_5)_2CO$.

ⓘ Not determined; background interference great.

ⓜ Calculation not meaningful.

ⓝ Residue weight same magnitude as blank.

ⓠ Interference likely (see Run 44 and note t).

ⓡ 0.012% (wt.) Pb via emission spectroscopy gives 10.1% Pb in benzene soluble.

ⓣ 3 ppm Pb via emission spectroscopy equivalent to 0.4% Pb in particulate.

V. DISCUSSION OF RESULTS

The results presented herein are based upon the generation, collection, and analysis of exhaust particles in a well defined system and under carefully controlled laboratory conditions. Initially, our challenge was to develop repeatable and reproducible means of generating, collecting, and analyzing exhaust particles. This required establishment of operational procedures which eliminated as many variables as possible, yet which provided an operational mode not uncommon to the automotive engine. Basic decisions with that in mind, dictated that initial studies be conducted using engines attached to laboratory dynamometer operated under carefully controlled conditions. A "conditioning sequence" with each test fuel was found to be necessary in order to stabilize engine emissions, deposits, and the exhaust system. The particle sampling operation under air diluted conditions at 60 mph road load provided a not uncommon operational mode for the engine and yet allowed particle sampling under conditions somewhat related to the actual vehicle emission environment on the roadway.

It is known that fuel composition and additives, particularly tetraethyl lead, effect automotive exhaust emissions, both gaseous and particulate. Initial experiments, then, dictated that a single fuel base be used and that TEL levels be varied in order to allow assessment of the validity and repeatability of the complete particulate investigation system. These studies were followed by an examination of the effect of lead scavengers, and then of various fuel additives. In all of these runs, a single engine type (Chevrolet 350 CID) was used. Following successful completion of this test sequence, we examined fuel composition effects and engine variation effects.

The next phase in the project dictated operation of actual vehicles with the same type engines, fuels, and operating conditions in order to establish the validity of the engine dynamometer studies. Subsequent vehicle studies examined the effect of cycled operation, cold starts, hot starts, mileage, and catalytic systems on emitted particulate mass and composition.

The objective, then, of this study has been to determine if fuel composition and fuel additives have a discernible effect on exhaust particulate mass and composition. When discernible effects were observed in carefully controlled dynamometer studies, the relationship to actual vehicles operated under realistic conditions was evaluated. Now that the basis upon which the data reported herein has been established, it is appropriate to address several specific topics.

The particulate sampling system, in this study the dilution tube and proportional samplers, is the key to the data generated in this study. In reality it dictates the definition of emitted exhaust particulate. We have found this "definition" to be critical, particularly with non-leaded fuel studies. We have operated the dilution tube system as a constant volume device, with all runs operating at the same total volume flow rate, to maintain isokinetic sampling in the sampling zone. As a result, specific dilution ratios vary depending upon whether we were sampling from one-half the engine under steady-state conditions (engine dynamometer studies) or operating in cycled mode with complete exhaust in the chassis dynamometer as noted in Table 12. As a result, the sampling temperature can vary substantially from run to run.

The impact of sampling temperature (dilution ratio) became apparent when non-leaded fuel vehicle studies began. In an attempt to quantify the magnitude of this effect, detailed sampling studies were conducted on Runs 29 and 31 (leaded [31] and non-leaded fuels [29]) using the total exhaust hot filter on one exhaust system from the right bank of cylinders and the dilution tube system on the other bank of cylinders. The results, shown in Table 45, clearly indicate that sampling temperature has a direct impact on the organic fraction associated with exhaust particulate.

TABLE 45

COMPARISON OF PARTICULATE COLLECTED WITH TOTAL EXHAUST HOT FILTER AND WITH THE ANDERSEN SAMPLER AFTER EXHAUST AIR DILUTION

		Hot Filter	Andersen Sampler*
Run 29			
	Emitted (gm/mile)	0.0026	0.0035
	Pb (wt. %)	9.0	4.3
	Pb (gm/mile)	0.000224	0.00015
	NH_3 content (relative amount/mg)	0	0.056
	HCl content (relative amount/mg)	0	0
	Aromatic content (relative UV absorbance per mg)	190	2700
	Benzene/methanol solubles (wt. %)	16.6	61
Run 31			
	Emitted (gm/mile)	0.0499	0.065
	Pb (wt. %)	48.5	51.9
	NH_3 content (relative amount/mg)	0	0.068
	HCl content (relative amount/mg)	0	0.023
	Aromatic content (relative UV absorbance per mg)	15	870
	Benzene/methanol solubles (wt. %)	<0.5	3.0

*Does not include large particles lost in dilution tube

In certain size fractions of emitted exhaust particulate, collected under air diluted conditions, the organic content from non-leaded fuel is as high as 70 percent. The implication seems obvious; exhaust particulate must be defined in terms of sampling temperature.

Further examination of the data for those runs in which both Andersen samplers operating at 1 cfm and a single total filter operating at 4 cfm were used indicated that the 4 cfm filter exhibits lower particulate mass collected. Examination of the temperatures at which these devices operate during a sampling run suggests that the same temperature-dependent phenomenon is occurring (Table 46) which is further noted in the emission rate calculation (Table 47).

TABLE 46

FILTER TEMPERATURE DURING SAMPLING RUN

Run No.	Dilution Tube Sampling Zone Temperature (°F)	Filter Temperature (°F) Andersen Back-up	Filter Temperature (°F) 4 cfm Filter
50	167.2	81.5	143.5
58	144.2	92.0	142.0
61	147.0	90.0	137.0
67	147.2	87.5	136.1

TABLE 47

MASS EMISSION RATES

Run No.	Particulate Mass Emissions (gms/mile) Andersen + Filter (1 cfm)	Particulate Mass Emissions (gms/mile) 4 cfm Filter
50	0.1565	0.1189
58	.0162	.0020
61	.0193	.0113
67	.1530	.1202

Obviously, much of the organic material associated with exhaust particulate is volatile at tailpipe temperatures and only becomes "particulate" after air dilution and cooling. The effect of dilution rates and filter face velocity has not been examined, although one might expect further effects there also.

In one study, Run 48, 4 cfm collection filters were stabilized at room temperature, the grams/mile particulate emission rate determined, and the filter then heated in an oven at various temperatures, cooled, reweighed, and heated to a higher temperature, etc. The results of this study are shown in Table 48. Again, the impact of organic levels is obvious.

TABLE 48

EMITTED PARTICULATE MASS ON 4 CFM FILTERS FOR RUN 48 AS A FUNCTION OF FILTER POST-COLLECTION TEMPERATURE TREATMENT IN OVEN

(Grams/Mile Emitted)

Run No.	Collected @ (°F)	Room Temp. Weight	100°F	150°F	200°F	250°F
48A	86	0.0605	0.0528	0.0468	0.0315	0.0213
B	89	.0519	-	.0383	.0204	.0196
C	80	.0554	.0502	.0349	.0221	.0170
D	77	.0494	.0460	.0383	.0247	.0221
E	85	.0460	.0443	.0340	.0221	.0204

A review of the data indicates that the temperature sensitivity during sampling is most significant using non-leaded fuels. True particulate emission rates and chemical characterization must involve definition of sampling temperature and collection device. Dilution ratio effects, at constant sampling temperatures, have not been examined herein although this factor may also be important and should be investigated.

It is apparent that a nearly "real" measurement of mass emission rate must be conducted using an air-dilution approach. Further, the air diluted exhaust sample must be as close to ambient temperatures as is practical. Techniques employed by Bergman(18) and Esso(19), and suggested by AMA fail to consider this important factor and, therefore, can be expected to exhibit mass emission rates significantly lower than when employing the techniques used herein and by Habibi(1).

The validity of the mass emission rates depends upon the fact that the proportional sampling devices in the sampling zone of the dilution tube are, indeed, taking a true proportional sample. Temperature flow-rate and mass profile data on the dilution tube have been presented in the Results Section. Mass profiles, under steady-state engine operation, are within 10 percent which is the factor which should appropriately be applied against the mass emission rate values calculated. Profiles during cyclic vehicle operation have not been conducted regarding mass distribution because no suitable real time mass monitor is available. Temperature and flow-rate, at a fixed position in the sampling zone, show relatively stable flow rates (CVS system) and temperature fluctuations consistent with vehicle cycle. Sampling during vehicle cyclic operation with the resultant temperature fluctuations add an additional complexity to the mass emission rate assessment due to the temperature effect factors noted above.

Comparison of total mass emission rates from Chevrolet 350 CID engines operated at 60 mph road load conditions on the engine dynamometer and in a vehicle on the chassis dynamometer, indicate that the vehicle emission rates are somewhat higher, even though sampling temperature and dilution ratio are quite different, due, no doubt, to the use of the complete exhaust in the vehicle study and only one-half the exhaust in the dynamometer study. Table 49 reviews the appropriate data.

TABLE 49

TOTAL MASS EMISSION RATES FROM CHEVROLET 350 CID ENGINES ON THE ENGINE DYNAMOMETER AND IN VEHICLES. MASS BY DILUTION TUBE PARTICULATE WEIGHT AND ANDERSEN SAMPLER - FILTER

Run No.	Equivalent/ Actual Mileage	Engine/Vehicle	Fuel	Mass Emissions (gm/mile)
22	4590*	Engine stand (70 Chev 350 CID)	AMOCO 91 RON 0 TEL	0.0132
21	4590*	Engine stand (70 Chev 350 CID)	AMOCO 91 RON 1/2 cc TEL/gal	.0187
23	4590*	Engine stand (70 Chev 350 CID)	Fuel A	.0910
43	2500	Vehicle (71) D1171	AMOCO 91 RON 0 TEL	.0115
58E	10,000	Vehicle (71) D1171	AMOCO 91 RON 0 TEL	.0162
45	3000	Vehicle (71) D1169	AMOCO 91 RON 1/2 cc TEL/gal	.0225
61	9100	Vehicle (71) D0234	AMOCO 91 RON 1/2 cc TEL/gal	.0193
27	7900	Vehicle (70) D0628	Fuel A	.1064
28	8260	Vehicle (70) D0628	Fuel A	.1196
50	3000	Vehicle (71) D1220	Fuel A	.1565

*Based upon equivalent 3150 miles during cycling, and one-half of 2880 miles during 48-hour, 60 mph road load sampling run.

Whether comparison between the 1970 and 1971 Chevrolet 350 engines is valid is not proven in this study. No significant engine changes were made, however. The major trends between non-leaded, low leaded, and fully leaded regular fuel appear to hold for the engine and vehicle studies.

Four vehicles have been run at selected mileages under steady-state cruise conditions (Table 50) and under cyclic conditions (Table 51). The data on mass emission rates are summarized in these tables.

TABLE 50

MASS EMISSION RATES FOR SELECTED VEHICLES WITH CONTROLLED FUELS AS A FUNCTION OF MILEAGE

(Mass Emissions via Dilution Tube Samples and Andersen/Filter)

Fuel	Vehicle No.	Run No.	Mileage	Total Mass Emissions (gm/mile)
AMOCO 91 RON	D1171	43	2,550	0.0115
0 TEL		58E	10,000	.0162
AMOCO 91 RON	D1169	45	3,000	.0225
1/2 cc TEL		61	9,101	.0193
Fuel C 91 RON	D0234	53	13,000	.0206
0 TEL		62	17,750	.0093
Fuel A	D1220	50	3,000	.1565
		67	9,286	.1930

Significant changes are noted for vehicle D1171 which exhibit an increase in particulate emissions, and for vehicle D0234 where a decrease is noted. Vehicle D0234 in Run 62 was barely operable and severe valve recession was observed when the engine was inspected. No significant change in particle MMED was observed in any of these comparisons.

TABLE 51

MASS EMISSION RATES FOR SELECTED VEHICLES WITH CONTROLLED FUELS AS A FUNCTION OF MILEAGE - CYCLIC OPERATION

(Mass Emission by 4 cfm Filter)

Fuel	Vehicle No.	Run No.	Mileage	Total Mass Emissions (gm/mile)	
AMOCO 91 RON 0 TEL	D1171	36	700	0.2019	FTP cold start, cold soak
				.0162	FTP, hot start
		46	3,770	.0507	
				.0409	FTP,
				.0426	cold start
				.0400	
				.0362	
				.0477	FTP,
				.0400	hot start
				.0353	
		58	10,000	.0196	FTP, cold start
				.0085	FTP, hot start
AMOCO 91 RON 1/2 cc TEL	D1169	48	4,250	.1214	FTP, cold start, cold soak
				.0554	FTP, cold start
				.0583	
				.0443	FTP,
				.0566	hot start
				.0468	
		60	9,101	.0690	FTP, cold start
				.0336	FTP, hot start
Fuel C 91 RON 0 TEL	D0234	53	13,000	.0617	FTP, cold start
				.0404	FTP, hot start
		62	17,750	.0217	FTP, cold start
				.0127	FTP, hot start
Fuel A	D1220	51	3,000	.2071	FTP, cold start
				.0813	FTP, hot start
		66	9,280	.1742	FTP, cold start
				.0988	FTP, hot start

The results are somewhat mixed, but there appears to be a trend toward decreased particle emissions with increased mileage for the non-leaded fueled vehicles under cycled conditions. The trend for low-leaded fueled vehicles is mixed depending upon cold or hot starting of the test sequence.

These tables also provide data which reflect the effect of cold start cycled tests vs. hot start on mass emissions. Data for many more runs of this nature are presented in the Results Section in Table 29. In all cases, except for Run 39A which was a catalyst equipped vehicle, cold start emissions are greater than hot start particulate emissions. It is suggested that the catalyst acts as a cold trap for volatile organics during cold start. These materials condense on the cold catalyst surface during start-up and are then oxidized as the catalyst reaches operating temperature. Such a theory would support the lower emission rate during cold start.

Several runs have been made comparing cycled vehicle operation mass particulate emission rates as a function of the cycle driven. A summary of this data is presented in Table 52.

TABLE 52

PARTICULATE MASS EMISSION RATES AS A FUNCTION OF VEHICLE CYCLE

(4 cfm Filter)

Run No.	FTP, Cold Start	FTP, Hot Start	LA-4, Hot Start
49	0.0911	0.0519	0.0516
		.0639	
51	.2071	.0813	.1091
53	.0617	.0404	.0708
58	.0196	.0085	.0108
60	.0690	.0336	.0466
62	.0217	.0127	.0068
66	.1742	.0988	.0605

In most cases, the LA-4 hot start cycle results in particulate emissions somewhat greater than the FTP hot start cycle but less than the FTP cold start cycle. LA-4 cold start tests were not run during this project because the FTP cold start cycle was used as the basis for cycled data comparison and vehicle scheduling did not allow the necessary soak period. In all probability, the LA-4 cold start would be somewhat higher than the FTP cold start emission rate. It is important to note that the FTP cycle was repeated sufficiently for 40 minutes vehicle operating time in order to obtain ample quantities for mass measurements. The LA-4 was run for the specified 23 minutes. As a result, the true mass emission rates under cold start conditions for one or two FTP cycles would likely be much greater than indicated herein. The LA-4 procedure, on the other hand, is of sufficient duration that the cold start probably will not have a severe impact on the particulate mass emission rate.

As noted earlier in this discussion, exhaust catalytic reactors have a pronounced effect on particulate emissions (when using non-leaded fuel, of course) during cold start vehicle operation. Table 53 presents other comparisons regarding catalyst effects.

The data suggests that particulate emission rates from new catalysts (Runs 41 and 56) exceed emission rates from non-catalyst equipped engines perhaps due to purging of loss material from the packed catalyst bed. Cold start particulate mass emissions are lower when using a catalytic reactor in the exhaust system. The effect of the catalytic reactor used in Run 56 on aldehyde emissions, as reported in the Results Section (Table 27), should also be noted here.

Further effects of catalytic devices and air/fuel ratios on particulate emissions and aldehyde emissions is reported under EPA Contract EHS 70-101 using similar engines and procedures to those used herein. In summary, the catalytic devices studied increased particulate emissions and substantially reduced aldehyde emissions. Lean air/fuel ratios result in somewhat higher particulate emission rates.

TABLE 53
EFFECT OF EXHAUST CATALYTIC REACTORS ON PARTICULATE EMISSION RATES WITH NON-LEADED 91 RON FUEL
(Packed Bed Proprietary Devices)

Run No.	Engine/Vehicle Data	Operational Mode	Particulate Emission (gm/mile)
With Reactor:			
39	71 Chev 350 CID Vehicle 61313 500 miles	FTP cycle, cold start	0.0059
			.0119
			.0144
		FTP cycle, hot start	.0068
			.0102
41	Vehicle 61313	60 mph - cruise	.0408
42	71 Chev 350 CID Vehicle 60337 53,000 miles	60 mph - cruise	.0088
56	70 Chev 350 CID* Engine	60 mph - cruise	.0292
Without Reactor:			
16	70 Chev 350 CID	60 mph - cruise	.01627
43	71 Chev 350 CID Vehicle 2,500 miles	60 mph - cruise	.0115
58E	71 Chev 350 CID 10,000 miles	60 mph - cruise	.0162

*Catalytic reactor was added to exhaust system after 75-hour stabilization sequence.

Only a limited evaluation of the effect of engine make is possible from the data generated. The basis for such a comparison is shown in Table 54. These data are from engine dynamometer tests with the fuel noted and suggested that the 1971 Pontiac 400 CID engine has significantly lower particulate emissions than the 1970 Chevrolet 350 CID engine. Limited data on the 1971 Chrysler 383 CID suggests that it is similar to the Pontiac engine in particulate emissions.

TABLE 54

EFFECT OF ENGINE MAKE ON PARTICULATE EMISSIONS ENGINE DYNAMOMETER TEST

Engine	Run No.	Fuel	Particulate Emitted (gm/mile)	MMED
70 Chev 350 CID	22	AMOCO 91 RON 0 TEL	0.0133	<0.1
	21	AMOCO 91 RON 1/2 cc TEL	.0187	<0.1
	23	Fuel Type A	.0910	<0.1
71 Pontiac	29/32	AMOCO 91 RON 0 TEL	.0032/.0031	!
400 CID	40	AMOCO 91 RON 1/2 cc TEL	.0114	0.37
	31	Fuel Type A	.065	∼0.1
71 Chrysler	59	AMOCO 91 RON 1/2 cc TEL	.01206	∼0.1
383 CID				

No realistic appraisal of engine make effect on particulate emissions from vehicles is possible. Many vehicles and makes have been examined using several fuels. The trends observed in the engine dynamometer studies are valid; i.e. higher lead content fuels result in higher particulate emissions. Eight 1969-1971 Chevrolet 350 CID engine vehicles operating on Fuel Type A have been evaluated. Mileages range from 3,000 to 35,000. Particulate emission rates at 60 mph cruise condition range from 0.1064 gm/mile to 0.1565 gm/mile, the average being 0.1299 gm/mile and the high value being from a 1971 low mileage vehicle.

During Runs 28 and 31, several particulate mass measurement techniques were evaluated. They included the total exhaust hot filter, a Beta-gauge/tape sampler, a Piezoelectric Crystal Monitor, the Andersen/filter combination at 1 cfm, and a 4 cfm total filter. The first three devices were provided by the Division of Chemistry and Physics, EPA. Tests were conducted under steady-state cruise conditions with engines and vehicles, and under vehicle cyclic operation. The results of this cooperative study have been presented in the Results Section and have been published(12). In general, the Andersen Sampler/filter provides the best measure of exhaust particulate mass emissions. The 4 cfm filter suffers from temperature and face velocity effects discussed earlier. The Beta-gauge approach provides an excellent mass measurement method for leaded fuels but its threshold sensitivity is too low for emissions from non-leaded fueled engines. The crystal monitor gave results consistently lower than all other techniques and was inoperable during cyclic vehicle operation. At this point in time, no device appears to be available to provide real time data on particulate emissions. The total exhaust hot filter suffers from the temperature effects discussed earlier but much more severely than does the 4 cfm diluted sample filter.

Nineteen particulate samples from nine runs using leaded gasoline showed 1.7 to 8.6 percent benzene solubles. In this discussion, the benzene soluble fraction is defined as that portion which was also soluble in methanol. Seven samples from four lead-free fuel runs ranged from 13.4 to 70 percent solubles. Run 34 is exceptional in showing 20.9 percent benzene solubles with a leaded gasoline; Run 34 was the only run employing a high performance, high octane requirement vehicle. Run 44 shows 2.4 percent benzene solubles when non-leaded gasoline was used; Run 44 was the only run utilizing non-leaded Fuel Type B.

The amounts insoluble in methanol ranged from 10 to 30 percent of the amount initially soluble in benzene. In some cases, the methanol insoluble material appeared to be an oil (i.e. Runs 22, 23, 34), having IR characteristics of an aliphatic hydrocarbon. In several other cases, the methanol insoluble fraction was soluble in acetone, producing a yellow coloration similar to the methanol soluble fraction, and is believed to be organic. The methanol insoluble fraction was generally insufficient for routine analysis.

Particulate samples of runs utilizing leaded fuels showed an acidity of 0.02 to 0.83 percent calculated as benzoic acid; the average was 0.37 percent for 21 samples excluding one exception of 7.8 percent. Five samples from runs without lead in the fuel ranged from 0.34 to 4.5 percent acidity, with the median value at 1.0 percent. Sawicki and Hauser(13) have shown that carboxylic acids are present in the benzene soluble fraction of air-borne particulates. The acidities of benzene and methanol soluble fractions ranged from 2 to 24 percent with the exception of the Type B fuel sample (Run 44) which showed 42 percent.

The phenolics of 28 pertinent particulate samples (17 runs) ranged from 0.01 to 1.8 percent calculated as p-phenylphenol.

Samples	Range, %
20	0.01 - 0.12
6	0.20 - 0.44
2	1.1 - 1.8

No distinction could be made based on the presence or absence of lead (TEL) or additives. The phenolics of the benzene and methanol soluble fractions range from 0.4 to 3.7 percent with the exception of the Type B fuel sample which was 17 percent. Gross(14) reports increased phenolic emissions in direct relation to fuel aromatics, which our studies tend to confirm.

The ultraviolet absorptivity of the benzene soluble fraction is considered to be a measure of aromatic but not aliphatic organic chemicals. Absorptivities can be related to the published knowledge of the ultraviolet absorbance characteristics of organic compounds. Absorptivity, earlier called extinction coefficient or specific extinction, is discussed in books by Scott(15) and by Friedel and Orchin(16). When the amount of benzene soluble fraction is too small for accurate measurement, the related values such as the relative ultraviolet absorbance/mg particulate or the ultraviolet absorbance of the total, collected particulate may be useful for comparative evaluations. The absorptivities of the benzene (and methanol) soluble fractions range from 3.5 to 53. Two possible correlations are observed. The aromaticity of the benzene solubles was lower (1) when Andersen samplers were employed in contrast to glass fiber filters, and (2) when lead (TEL) was omitted in the fuel used.

Thus with the Andersen post filters, samples from runs containing leaded fuels showed values of 12 to 42 (Runs 23 and 31) whereas samples from non-leaded fuels showed values of 3.9-7.2 (Run 29). With glass filters, the corresponding values with lead were 21 to 53 (Runs 19, 20, 23, 24, 25, 28, 31, 34, 40, with 15 excepted). Corresponding values without lead were 16 to 29 (Runs 22, 29, 53, with 44 excepted).

Runs 24 and 25 are the only duplicate engine runs listed in the tables. Runs 22, 24, and 25 were the only runs for which replicate particulate samples were collected during the run and subsequently analyzed. An indication of reproducibility, maximum deviations, expressed as percent of the mean (average), were calculated for the duplicates as follows:

TABLE 55

ENGINE RUN AND ANALYTICAL METHOD REPRODUCIBILITY ANALYSIS OF FIBERGLASS FILTER PAPERS EXPRESSED AS PERCENT OF THE MEAN

		Engine Run Repeatability	Filter Paper Repeatability
In particulates,	benzene solubles	14%	6%
	acidity	46%	41%
	phenolics	20%	33%
In benzene soluble fractions,			
	absorptivity	5%	3%
	acidity	37%	39%
	phenolics	20%	20%

The deviations indicate that the acidity measurements are less precise than the others, possibly because trace acid contamination is more likely. The precision is best for the percent benzene solubles and absorptivity because milligram amounts are utilized; the analyses of phenolics and acidity utilize microgram amounts.

Hangebrauck et. al. analyzed for polynuclear aromatics in exhaust particulates, and calculated reproducibility as 42-55 percent as percentage of the mean(17).

If the experiments and analyses are conducted to help attain a more desirable ecology, then the precision is deemed adequate to detect significant changes (i.e. two-fold and greater). Precision can be improved by processing larger samples, or by using averages of multiple determinations.

The Gelman, Type A, glass fiber filter (61698, pure grade, 0.3μ, 142 mm) is considered the best of those studied for the analysis of organics. The residues obtained via benzene extraction of the blank filters amounted to 0.4 ± 0.25 mg with absorptivities of 2.1 ± 1 at 255 nm.

The results obtained using the Millipore filter AAWP, 0.8μ are unsatisfactory because the benzene soluble residues of blank filters ranged from 25 to 30 mg, often exceeding the weights of the residues obtained by benzene extraction of filters containing particulates. The blank residues had absorptivities ranging from 0.6 to 0.8 at 25 nm, attributed to a tailing effect of an intense absorbance doublet at 275 and 285 nm.

The UV absorbance and fluorescence values tend to give similar variations on all the samples. In general, the smaller particles have the highest concentration of detectable organic material present. The concentration also increases when non-additive gasolines are used; however, the total particulate is also decreasing and, therefore, the total detectable organics in a given size range do not vary significantly with additive. The tube sweeping samples indicate an increase in organics at a further distance down the tube from the engine, while the slit samples contain very low organic levels, which may be due to the low contact with exhaust fumes. The fluorescence curves may be the most useful in the future in correlating to actual percentage amounts of various classes of organic compounds, since spectra have been obtained at excitation wavelengths of 290, 330, and 353mμ.

The Relative UV Fluorescence (RF) value was assumed to be proportional to the poly-nuclear content (i.e. anthracene and higher); however, this point has not been established experimentally in this series.

Samples from six Andersen impingement filter plates of Runs 21 and six from Run 22 were analyzed according to the UV procedure described earlier but modified to measure only those dilutions when the ultraviolet absorbance at 255 nm is less than 0.4 to minimize fluorescence quenching. The RF must be compared to particulate weight, benzene soluble fraction, or the Relative Ultraviolet (RU) value for correlation and other uses of the analyses. The concept of the RF and RU values was devised for small amounts (i.e. <10 mg) of collected particulates.

The RU value is considered a relative measure of aromatics in particulate extracts; absorbance values are proportional to concentration. The RF value is considered a relative measure of poly-nuclear aromatics (PNA). The ratio RF/RU could be a relative measure of the ratio of PNA to total aromatics. If both RU and RF values are proportional to concentration, then the ratios RF/RU and RU/RF will be constant at different dilutions.

Plotting data for Runs 19 and 20 as shown in Figures 79 and 80 illustrate two points: 1) The ratios of RU/RF changed markedly upon further dilution of the extracts of Plates 1 and 6, Run 20. 2) The ratio RU/RF of all extracts decreases proportionally with the dilution as measured by absorbance. These results can be explained by fluorescence quenching at higher concentrations. The established technique for minimizing quenching is to make measurements in solutions of greater dilutions.

Figure 79

Ratio RU/RF as Function of A255
Run #20
Extracts of Andersen Plate

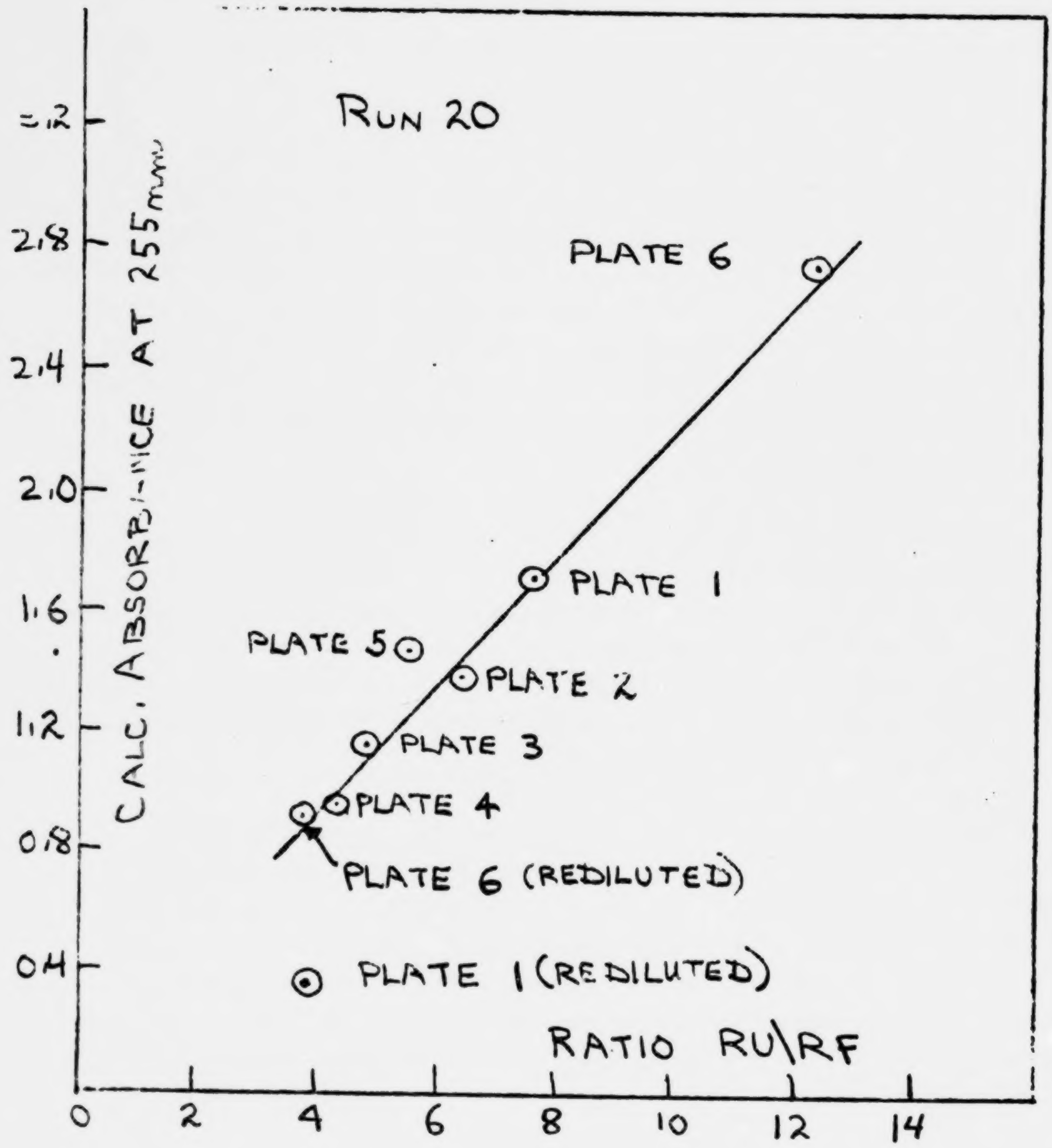
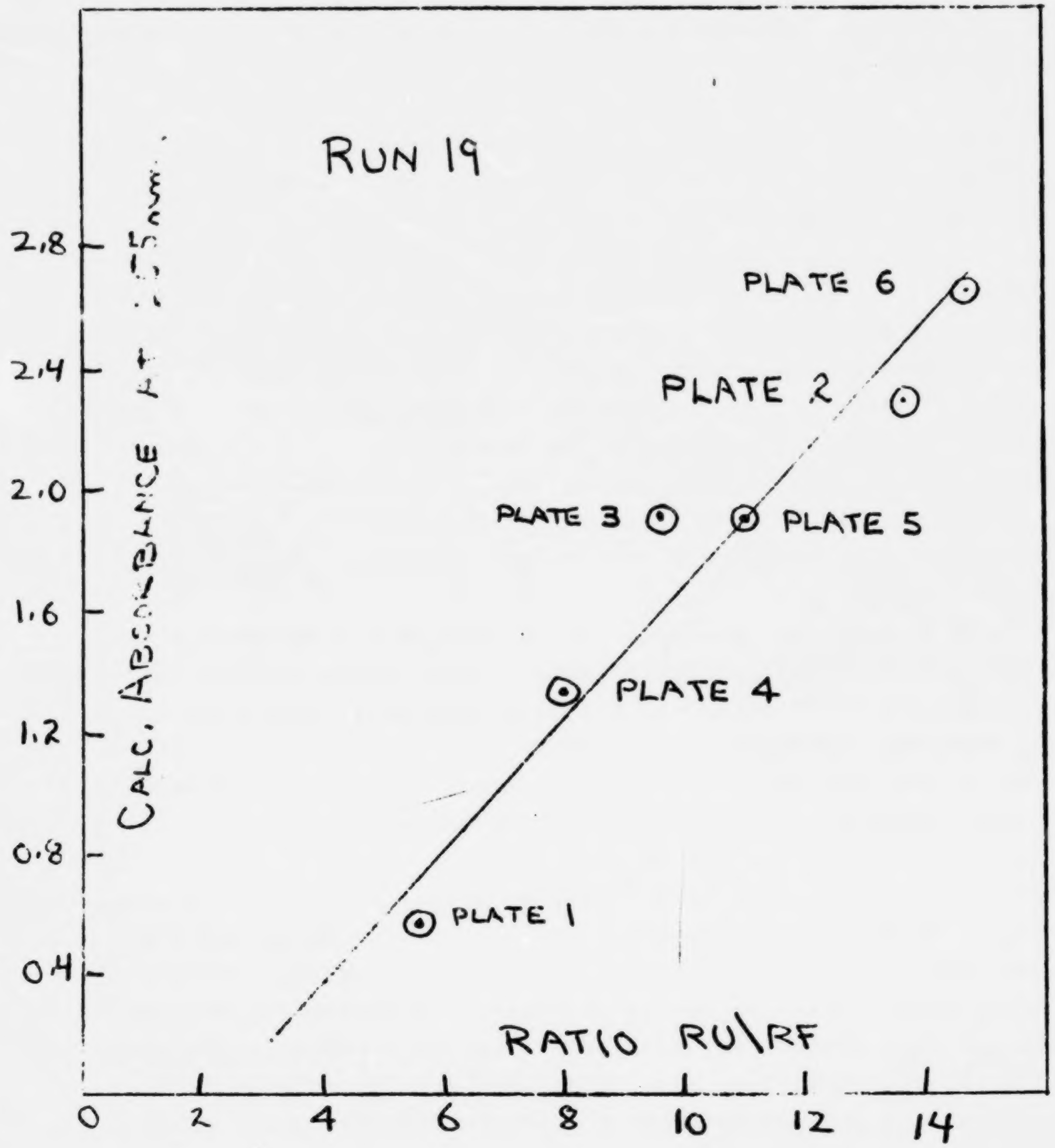


Figure 80

Ratio RU/RF as Function of A255
Run #19
Extracts of Andersen Plate



Figures 81 and 82 illustrate the corresponding ratios for Runs 21 and 22 when the absorbance at 255 nm of the solutions measured was kept below 0.4. In each run, with the exception of Andersen stage 1, the ratios are considered to be constant (i.e., 2.6 ±0.4 and 2.9 ±0.2).

The ratios were plotted as RU/RF in the figures to emphasize quenching; the ratios are given as RF/RU in Table 56 to be proportional to fluorescence content.

Assuming that the ratios of RF/RU listed in Table 56 are meaningful, the following conclusions can be made:

a) The largest particulates (Plate 1) contain a smaller ratio of PNA's to total aromatics present.
b) No significant differences in the ratios for particulate sizes represented on Plates 2 through 6.
c) The differences in the ratios observed between Runs 21 and 22 are considered insignificant.

The levels of carbonyl compounds, calculated as benzophenone equivalents, were less than percent in all particulate samples examined. Comparisons and correlations with engine operating conditions could not be made with confidence below this level. Accuracy is limited because of the high solvent and filter blanks. Reducible chemicals other than carbonyls are potential interferences.

Time did not permit checking the polarographic analyses using established methods. The polarographic responses are based on measurement of reducible, chemical species and are characterized by specific, half-wave potentials. Aliphatic carbonyls and aromatic aldehydes in general give useful responses only after conversion to the hydrazones by addition of hydrazine. Lead salts and aromatic ketones such as acetophenone and benzophenone give measurable responses without hydrazine.

Figure 81

Ratio RU/RF as Function of A255
Run #21
Extracts of Andersen Plate

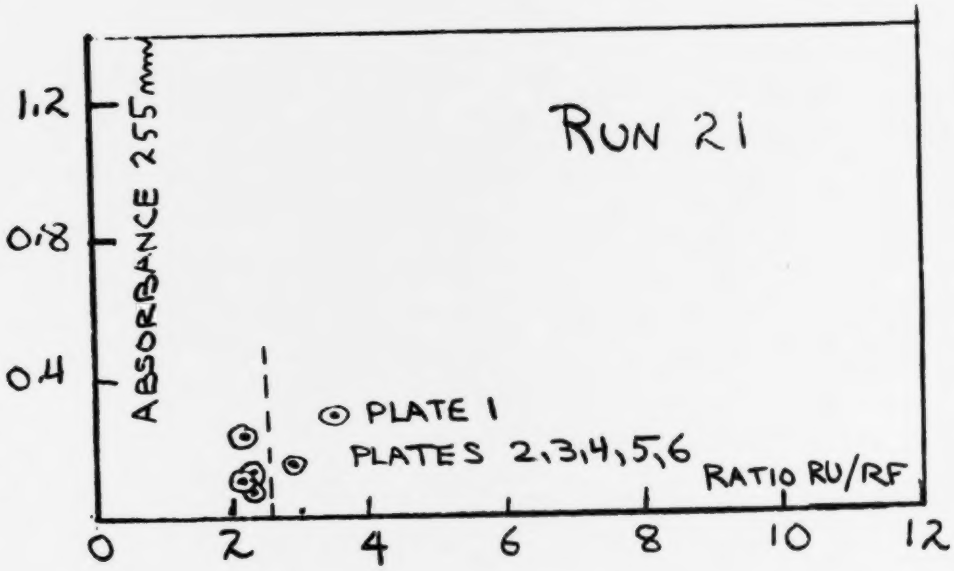


Figure 82

Ratio RU/RF as Function of A255
Run #22
Extracts of Andersen Plate Filters

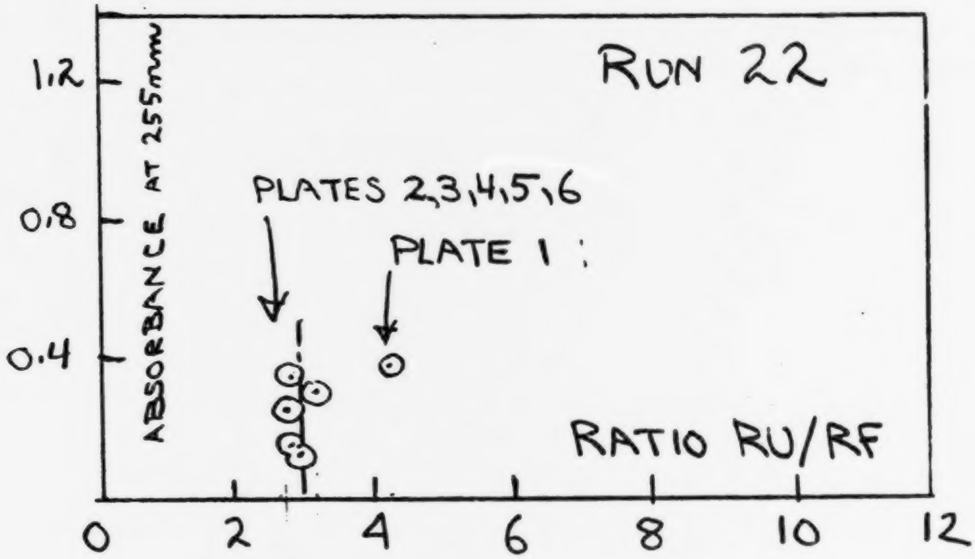


TABLE 56
ANALYSES OF RUNS 21 AND 22

Run	Andersen Plate	Sample Wt. (mg)	Relative Ultraviolet (RU) Value	Relative Fluorescence (RF) Value	Ratio RF/RU
21	1	2.12	1330	375	0.28
	2	2.00	850	295	0.35
	3	1.39	719	332	0.46
	4	1.10	1000	442	0.44
	5	0.44	1909	805	0.42
	5	0.61	3607	1631	0.45
22	1	0.62	6242	1484	0.24
	2	0.40	3175	1105	0.35
	3	1.00	1730	611	0.35
	4	0.95	1684	608	0.36
	5	1.16	2250	824	0.37
	6	0.90	3591	1139	0.32

Note

Fluorescence determined with solutions diluted so that the ultraviolet absorbance at 255 nm <0.4.

In this work a maximum of 2 ml of methanol solutions of the benzene soluble residue was available for polarographic analyses. The results are expressed in amounts of representative compounds for each class rather than mole percentiles. Thus aliphatic carbonyls are calculated as acetaldehyde, even though this volatile compound is not expected in particulate samples. Responses for aliphatic ketones (limit, 25 μg/ml calculated as acetone) and zinc salts (limit, 10 μg/ml) were not observed in the samples examined.

The response for formaldehyde is fairly specific; its presence in some particulate samples could be accounted by the oxidation of micro amounts of the methanol solvent. Benzophenone was chosen as a calibration standard because prior spectroscopic work after formation of the 2,4-dinitrophenylhydrazones indicated the carbonyls to be more similar to the aromatic rather than aliphatic ketones.

At lower levels, zinc salts could interfere in the determination of benzophenone.

An unsuspected finding was the presence of lead compounds in the methanol solutions of the benzene soluble fraction when leaded fuel was used. Thus the benzene soluble fraction of Run 40 showed 10.1 percent Pb by emission spectroscopy and 13.9 percent via polarography. The benzene solubles from eight out of nine runs utilizing leaded gasoline showed polarographic responses equivalent to 2-14 percent lead; the limit of detection in the ninth run was 1.5 percent. Corresponding analyses of Runs 22 and 44 (non-leaded) showed a 0.9 percent (polarography) and 0.4 percent (emission spectroscopy) respectively.

Polarographic analysis of the sample collected during Run 44 indicated the presence of an interfering material equivalent to 56 percent Pb. Thus the high lead content of Run 31 is questionable. The values for lead via polarography should be considered maximal. Emission spectroscopy is superior when only the lead content is desired.

Lead was not detected in the blanks from unused filters and the benzene solvent. The lead response could not be measured polarographically when Millipore filters were used because an excessive background signal was observed. The percent Pb in the benzene solubles was calculated as follows:

$$\% \text{ Pb} = \frac{V \times W_{Pb}}{W_s \times 10}$$

where

W_{Pb} is the response for Pb calcualted as µg/ml
W_s is the amount of benzene soluble residue, mg
V is the amount of methanol in ml used to dissolve W_s

Values of percent Pb were not calculated for samples containing less than 1 mg/5 ml benzene solubles because the detection limit in these cases would be 3 percent.

It has been suggested that the UV absorptivity at 255 nm of the benzene soluble residue can be used as a measure of aromaticity. $PbBr_2$ has an absorptivity of 16.6 at 255 nm. Thus the presence of lead compounds can alter the absorptivity and produce an erroneous measure of aromaticity. Measurement of the absorptivity at 300 rather than 255 nm would minimize the interference of lead compounds in measuring aromaticity.

It should be readily apparent at this point, that detailed in-depth analysis of particulate material collected from each and every experimental run was not conducted. Experimental runs and subsequent analyses were designed consistent with attempts to ascertain significant factors and detailed analysis of selected samples, as much as to develop and critique the analytical procedure. Complete analysis of a single vehicular cycled run would be literally impossible because of lack of sufficient sample, even when using leaded fuels. The report, does, however, provide meaningful general examination and details of particulate emissions with sufficient and appropriate examination of key variables, as they become apparent, to warrant its use as the basis for detailed future studies.

VI. FUTURE

This research program has attempted to quantify the key factors associated with the generation, collection, and analysis of exhaust particulate as related to fuel factors and additives therein. As is usual in ventures of this nature, research generates many more questions than it answers. It is obvious that much additional time and money can be spent analyzing exhaust particulates and, indeed, such may be necessary in the future.

A key factor, however, before meaningful work can be conducted by various groups is the examination of the effects of the generating and collection procedures on exhaust particulate. Real-world exhaust particulate assessment is nearly impossible and certainly impractical. On the other hand, examination of tailpipe particulate emissions is clearly misleading.

Further efforts must be directed toward defining key generation and collection aspects of the exhaust particulate problem so that nearly-real assessments of fuel factors, additives, and devices can be made.

Such efforts will, simultaneously, provide the appropriate technical review necessary for the meaningful application of an exhaust particulate emission standard from motor vehicles, if such is employed in the future.

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PART 2

I. CONCLUSIONS

1. Exhaust particulate mass emission rates are a function of mode of vehicle operation. They increased with test mode in the following order: 60 mph steady state < 41 minute cold start LA-4 cycle < 23 minute cold start LA-4 cycle.

2. Low-leaded fuel consistently afforded higher particulate mass emission rates than did non-leaded fuel.

3. The mass median equivalent diameter of exhaust particulate is a function of vehicle operation mode. It increased with test mode in the following order: 60 mph steady state < 41 minute cold start LA-4 cycle < 23 minute cold start LA-4 cycle over the range of 0.54-9.0 microns.

4. Of the particulate filtering systems employed, the highest mass emission rates were detected by an Andersen Impactor with back-up 142 mm Millipore filter operating at 1 cfm. Successively lower mass emission rates were obtained by use of parallel 142 mm Gelman glass fiber filters operating at 1 cfm and 4 cfm.

5. An increase in dilution tube flow rate from 350 to 500 cfm did not result in any significant trend in observed particulate mass emission rate. However, it did effect an overall increase in the mass median equivalent diameter of collected particulate and in the concentration of trace metals associated with the collected exhaust particulate (500 cfm rates being the higher).

6. Cooling of air ahead of the dilution tube inlet resulted in an increase in both the observed particulate mass emission rates and the concentration of particulate associated benzo-α-pyrene. A corresponding decrease in particule MMED for non-leaded fuel was observed. In general, this cooling also resulted in a lower concentration of particulate associated trace metals.

7. Cooling of the air diluted exhaust effluent by means of a heat exchanger within the dilution tube resulted in a decrease in the observed mass emission rates for particulate matter. No significant trends were obvious for the effect of this variable on particulate concentrations of either benzo-α-pyrene or trace metals.

II. EXPERIMENTAL PROCEDURE

A. FUEL CHARACTERIZATION

Samples of some 30 different commercially available gasolines were procured from three different geographic areas of the United States. These areas - New Jersey, Los Angeles, and Detroit - were selected in order to afford samples of gasoline which had been refined from at least two different base stocks.

The samples were collected in 5 gallon mild steel cans which were rinsed with 1 gallon of the specific fuel to be analyzed prior to filling. In order to assure that metal pick-up from the cans was not contributing to the trace metal analyses which were performed on each sample, research grade fuel was stored in one of the cans for a period of one week and then subjected to analysis for trace metal content as a control.

A list of the fuels procured, their geographical origin, advertisied RON and lead content is shown in Table 57.

Each sample was subjected to analysis for RVP, distillation, RON, MON, and FIA composition using standard ASTM Procedures*. In addition each gasoline was analyzed for trace metals, lead, sulfur, phosphorus, aldehydes, chlorine and bromine, carbon and hydrogen, and benzo-α-pyrene using the standard analytical methods which have been described earlier in this report.

B. EVALUATION OF DILUTION TUBE VARIABLES ON THE COLLECTION OF EXHAUST PARTICULATE MATTER

Using the Dow dilution tunnel described in detail on page 18 of this report, a series of tests were conducted to evaluate the effects of several dilution tube variables on the collection and nature of automotive exhaust particulate.

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*ASTM Procedures D323, D86, D908, D357, D1319

TABLE 57
GASOLINE SAMPLES IDENTIFICATION

Sample No.	Location	Stated RON	Stated Lead Content
1	Detroit	94	3 cc/gal
2	Detroit	94	3 cc/gal
3	Detroit	94	3 cc/gal
4	Detroit	94	3 cc/gal
5	New Jersey	94	3 cc/gal
6	New Jersey	94	3 cc/gal
7	New Jersey	94	3 cc/gal
8	New Jersey	94	3 cc/gal
9	Los Angeles	94	3 cc/gal
10	Los Angeles	94	3 cc/gal
11	Los Angeles	94	3 cc/gal
12	Los Angeles	94	3 cc/gal
13	Detroit	100	3 cc/gal
14	Detroit	100	3 cc/gal
15	Detroit	100	3 cc/gal
16	New Jersey	100	3 cc/gal
17	New Jersey	100	3 cc/gal
18	New Jersey	100	No lead
19	Los Angeles	100	3 cc/gal
20	Los Angeles	100	3 cc/gal
21	Los Angeles	100	3 cc/gal
22	New Jersey	94	0.5 cc/gal
23	Los Angeles	94	0.5 cc/gal
24	Detroit	91	0.5 cc/gal
25	New Jersey	91	0.5 cc/gal
26	Los Angeles	91	0.5 cc/gal
27	Detroit	91	No lead
28	Detroit	91	No lead
29	New Jersey	91	No lead
30	Los Angeles	91	No lead

Exhaust particulate matter was generated using two 1971 Chevrolet Impalas operating on the chassis dynamometer, each fitted with identical 350 CID V-8 engines. These vehicles had been utilized in the earlier part of the contract effort. One vehicle was operated on Indolene 0 91 RON non-leaded fuel, and the other on Indolene 5 91 RON fuel containing 0.5 cc TEL/gallon in combination with 0.2 theoretical equivalents of EDC and 0.07 theoretical equivalents of EDB.

Each test vehicle was operated on the Clayton chassis dynamometer and the total exhaust fed into the Dow dilution tube described in detail in Phase I of this report.

Air diluted exhaust particulate was collected identically utilizing sample probes located at the end of the exhaust inlet and connected to two parallel 142 mm Gelman glass fiber filters operating at 1 cfm, one 142 mm Gelman glass fiber filter operating at 4 cfm, and an Andersen 6-stage impactor with back-up 142 mm Millipore filter operating at 1 cfm. This type of collection system has been described in detail earlier in this report (see page 21).

A series of baseline tests were performed on each vehicle. Particulate matter was generated and collected under the following vehicle operating sequences:

a) 60 mph road-load, steady state - 2 hours
b) 23 minute LA-4 cycle (cold start)
c) 41 minute modified LA-4 cycle (cold start)

The total flow rate through the dilution tube was adjusted to 350 cfm prior to each test run being initiated with the vehicle shut down. In each test the following particulate characteristics were determined: mass emission rate (gm/mile), mass size distribution, and polynuclear aromatic content determined as benzo-α-pyrene. Attempts to determine the organic content of the collected particulate matter by carbon and hydrogen analysis failed because insufficient sample was available to afford meaningful data. In all test runs trace metal analyses were also performed on the particulate matter collected on the 142 mm Millipore filter used as a back-up to the Andersen impactor. In those runs utilizing low lead fuel, a lead determination was made on the particulate matter collected on the various stages of the Andersen impactor. The above analytical scheme was used throughout this investigation of particulate sampling parameters. The analytical procedures utilized have been described in detail in Phase I of this report.

On completion of the baseline testing, the following series of tests were conducted:

1. Variation of Dilution Tube Flow Rate
Tests b) and c) above were repeated with the total flow rate through the tube adjusted to 500 cfm for both the leaded and non-leaded vehicles. Again this flow rate was established prior to each test sequence with the vehicle shut down.

2. Effect of Dilution Air Cooling
A series of experiments were performed to determine the influence of dilution air cooling on collected exhaust particulate matter. Three approaches were utilized; cooling within the dilution tube, cooling of diluent air ahead of the dilution tube, and use of diluent air when the ambient temperature was less than 40°F.

In order to effect cooling of the air-diluted exhaust effluent within the dilution tunnel, a heat exchanger was designed in such a way that it offered a maximum surface area for cooling yet provided the least opportunity for particle trapping by impingement. To accomplish this, two 48" x 29" x 1/16" mild steel plates were fitted each with 40 feet of 1/4" ID copper tubing which was looped back and forth over their surface. The tubes were welded to the plates at intervals of approximately

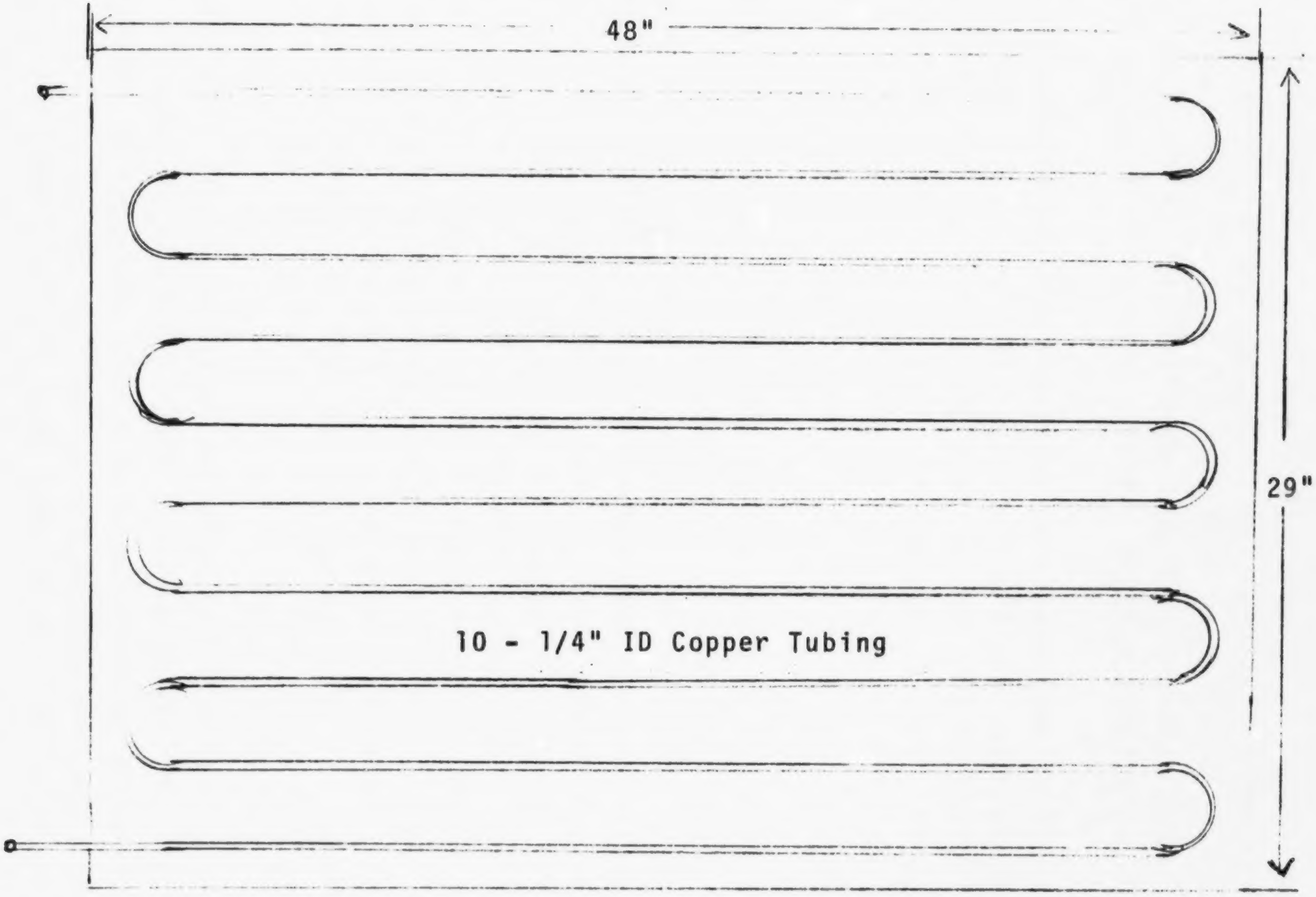
1 inch along their length (see Figure 83). The plates were then bent along their width to form two concentric cylinders which were separated by 2-inch metal spacers. This assembly was mounted in the dilution tube at a point 4 feet downstream of the exhaust inlet and held in position by a second set of 2-inch spacers fitted to the inside wall of the dilution tube. A schematic of the heat exchanger is shown in Figure 84. This arrangement assured a minimum interference with the flow pattern of diluted exhaust effluent within the dilution tube.

The effect of this device on collected particulate matter was determined with both air and water passing through the cooling coils during 60 mph steady state and 23 minute LA-4 cycle (cold start) vehicle operation. Runs were conducted with the total air flow through the dilution tube adjusted to both 350 cfm and 500 cfm prior to vehicle start-up.

In a second set of experiments, the heat exchanger was removed and an automotive radiator attached to the dilution tunnel immediately ahead of the air inlet filter. Passage of water through this device permitted cooling of inlet air prior to its entry into the dilution tube. The effect of cooling the dilution air in this manner on the collected particulate matter was investigated with the test vehicles operating at 60 mph steady state (2 hours), in the 23 minute LA-4 cycle (cold start), and in the 41 minute modified LA-4 cycle (cold start). These tests were also run with the total dilution tube flow rate adjusted to both 350 cfm and 500 cfm prior to vehicle operation.

A final series of tests intended to ascertain the effect of dilution air temperature on collected exhaust particulate was conducted in the absence of a heat exchanger by drawing dilution air from outside the dynamometer facility, which had an ambient temperature of less than 40°F just before the

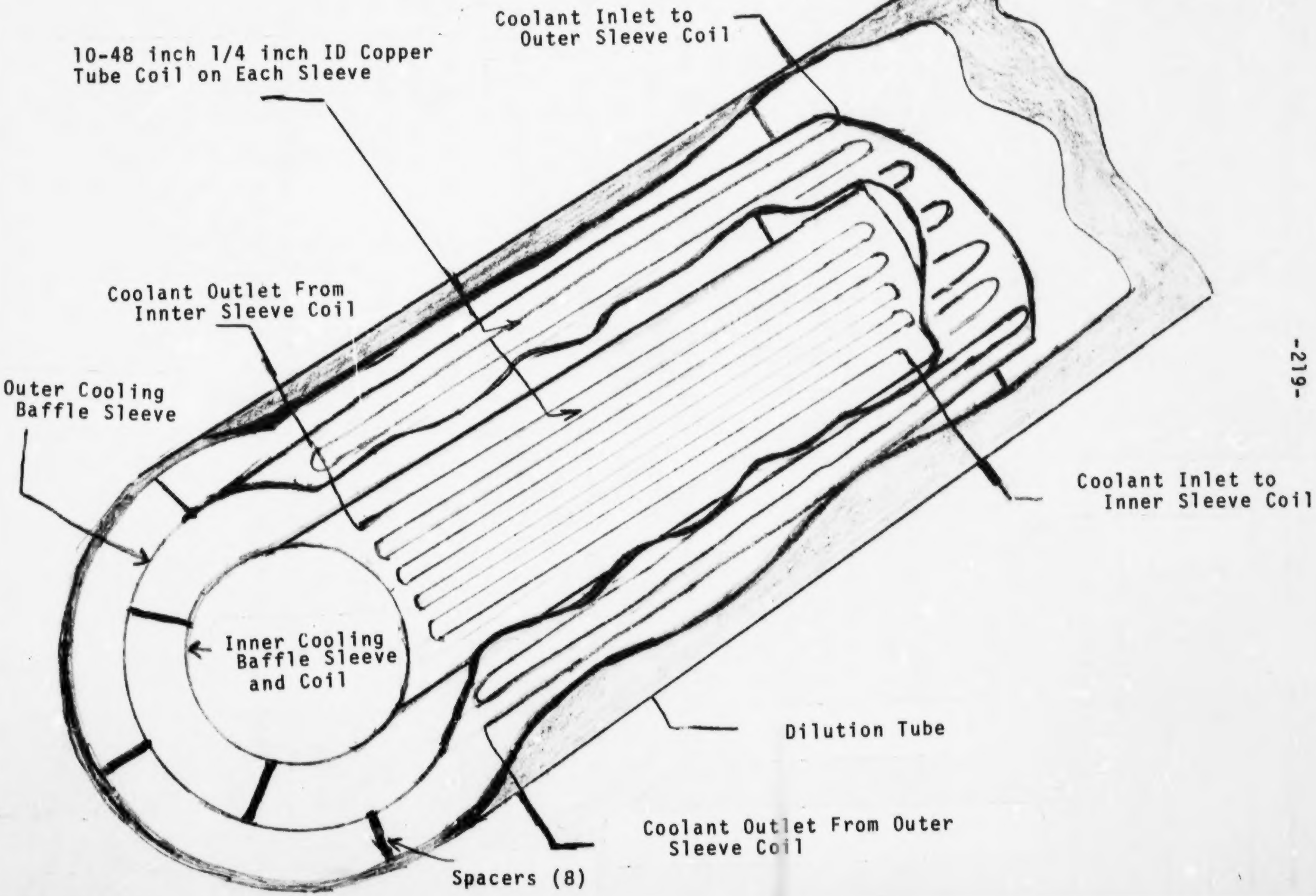
FIGURE 83


48"
29"
10 - 1/4" ID Copper Tubing

DILUTION TUBE COOLING BAFFLE

FIGURE 84

CUT-AWAY VIEW OF COOLING SLEEVE
INSIDE OF DILUTION TUBE


Coolant Inlet to Outer Sleeve Coil
10-48 inch 1/4 inch ID Copper Tube Coil on Each Sleeve
Coolant Outlet From Innter Sleeve Coil
Outer Cooling Baffle Sleeve
Coolant Inlet to Inner Sleeve Coil
Inner Cooling Baffle Sleeve and Coil
Dilution Tube
Coolant Outlet From Outer Sleeve Coil
Spacers (8)

Dri-Pak filter. These latter experiments were run with the vehicles operating at 60 mph steady state (2 hours), in the 23 minute LA-4 cycle (cold start), and in the 41 minute modified LA-4 cycle (cold start). The total flow rate through the tube was adjusted to 350 cfm prior to each test run.

Figure 85 shows a complete test matrix for the above set of experiments.

C. EVALUATION OF A BETA-GAUGE PARTICULATE MASS MEASURING DEVICE

A series of test runs were performed to correlate the exhaust particulate mass measuring efficiency of a prototype Beta-gauge compared with the conventional collection techniques utilized throughout the major part of this contract effort.

The Beta-gauge device evaluated was developed by the Industrial Nucleonics Corporation of Columbus, Ohio, under Environmental Protection Agency Contract No. 68-02-0210. A detailed description of the device can be found in the Final Report published under this Contract in February 1972. Collection of exhaust particulate within the device was accomplished by drawing a proportional sample of air-diluted exhaust effluent from the Dow dilution tube through a Pallflex E70/2075W filter pad having a cross-sectional area of 3 sq cm. The sample probe for the Beta-gauge was located at the end of the dilution tube remote from the exhaust inlet and adjacent to the probes used to feed the conventional filtering equipment (see Figure 2).

The following three vehicles operating on a chassis dynamometer were used to generate the exhaust particulate:

FIGURE 85

EVALUATION OF DILUENT AIR TEMPERATURE ON THE COLLECTION OF EXHAUST PARTICULATE MATTER

TEST MATRIX

Cooling Mechanism	Dilution Tube Flow Rate	Test Conditions*
Internal Heat Exchanger:		
Air cooled	350	A, B
Water cooled	350	A, B
Water cooled	500	A, B
External Heat Exchanger:		
Water cooled	350	A, B, C
Water cooled	500	A, B, C
Ambient Air <40°F	350	A, B, C

*A = 60 mph steady state
B = 23 minute LA-4 cycle (cold start)
C = 41 minute modified LA-4 cycle (cold start)

1971 Chevrolet Impala - 350 CID V-8 - Indolene 0 fuel
1971 Chevrolet Impala - 350 CID V-8 - 0.5 cc/gallon leaded fuel
1971 Chevrolet Impala - 350 CID V-8 - 3.0 cc/gallon leaded fuel A*

These were operated under a variety of steady state conditions on the chassis dynamometer and were also tested in the 23 minute LA-4 cycle (cold and hot start) and in the California 7 mode cycle. For comparison purposes, two parallel proportional filters were employed in this part of the program: a 142 mm Gelman glass fiber filter operated at 4 cfm, and a 47 mm Gelman glass fiber filter operated at 3.29 cfm. In one run (see Results Section) the Beta-gauge unit was operated in such a way that the face velocity of air diluted exhaust through it was equivalent to that in the 47 mm filter. This approach then allowed a direct comparison of particulate mass emission rates as detected by both the Beta-gauge and proportional filters for a variety of different fuels and vehicle operating sequences.

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*See page 85 of Phase I.

III. EXPERIMENTAL RESULTS

A. FUEL CHARACTERIZATION

Physical and chemical analyses of the thirty commercial gasoline samples procured are shown in Tables 58, 59, 60, and 61.

B. EVALUATION OF DILUTION TUBE VARIABLES ON THE COLLECTION OF EXHAUST PARTICULATE MATTER

Tables 62 and 63 show the mass emission data obtained during those test runs intended to determine the effects of dilution air cooling and dilution tube flow rate on the physical and chemical character of exhaust particulate matter. Also included is temperature data obtained in each run for the raw exhaust immediately ahead of the dilution tube, dilution air immediately prior to exhaust mixing, diluted exhaust at the sampling zone and in the 1 cfm filter. The latter temperature was measured a few millimeters above the filter pad surface. In the steady state runs the dew point within the filter units is also presented. This was determined by direct measurement of the relative humidity and temperature of the air diluted exhaust effluent at the sampling zone of the dilution tube and subsequent use of psychrometric tables. Data generated by Dow under Environmental Protection Agency Contract EHS-70-101 suggests that a filter temperature of less than 20°F above the dew point can lead to condensation of water within the filters and erroneous mass emission data.

Tables 64 and 65 present data for the lead and benzo-α-pyrene (BaP) content of the particulate matter collected.

Finally, Tables 66 and 67 show trace metal analyses for the particulate matter collected on the back-up Millipore filter used in each of the test runs.

TABLE 58

PHYSICAL ANALYSES OF GASOLINE SAMPLES

	1	2	3	4	5	6	7	8	9	10	11	12
API Gravity	63.8	65.5	62.2	60.7	64.0	61.2	64.1	63.0	59.1	58.3	60.1	60.4
Distillation:												
IBP	88	74	88	84	94	78	84	88	88	96	80	96
5	104	86	100	100	106	93	98	112	108	102	98	112
10	106	95	110	111	116	104	111	120	118	124	110	122
20	140	114	136	136	140	128	128	148	146	148	138	144
30	150	138	160	166	162	153	150	176	172	169	169	162
40	192	163	186	190	190	182	169	200	194	200	192	184
50	214	184	216	216	210	216	192	222	212	232	222	202
60	238	212	252	246	242	244	224	248	236	262	264	228
70	264	240	288	276	274	282	261	172	262	298	290	266
80	300	276	306	302	320	311	300	304	290	340	324	300
90	350	336	342	352	342	356	344	340	346	380	360	362
95	362	386	385	392	378	382	385	362	398	400	381	388
EP	378	401	424	420	412	414	408	390	414	422	412	424
% Recovery	95.0	97.0	95.0	96.0	95.5	96.0	97.0	95.0	97.5	95.5	96.0	95.5
% Residue	0.4	0.8	0.6	0.5	0.8	0.8	0.8	1.0	0.6	0.6	0.8	0.8
% Loss	4.6	2.2	4.4	3.5	3.7	3.2	2.2	4.0	1.9	3.9	3.2	2.7
RON	92.8	91.2	92.0	93.1	91.7	93.8	93.5	91.9	93.3	91.5	91.2	93.6
MON	84.2	87.2	86.3	87.0	85.7	86.0	85.6	85.6	84.4	83.7	84.7	85.0
RVP	13.2	14.0	13.0	12.9	12.6	13.5	12.8	12.3	11.3	11.1	12.6	10.1
FIA:												
% Saturates	66.5	78.9	70.7	70.7	70.7	60.8	64.8	69.1	71.7	64.3	71.0	72.2
% Olefins	16.0	7.1	7.4	7.4	11.7	13.7	16.0	10.6	5.2	6.7	8.6	8.1
% Aromatics	17.5	14.0	21.9	21.9	17.6	25.5	19.2	20.3	23.1	29.0	20.4	19.7
Stated RON	94	94	94	94	94	94	94	94	94	94	94	94
Stated Lead Content (cc/gallon)	3	3	3	3	3	3	3	3	3	3	3	3
Source*	D	D	D	D	N	N	N	N	L	L	L	L

*D = Detroit N = New Jersey L = Los Angeles

TABLE 59

PHYSICAL ANALYSES OF GASOLINE SAMPLES

	13	14	15	16	17	18	19	20	21
API Gravity	60.5	65.9	59.9	59.2	65.4	56.3	56.7	55.4	58.3
Distillation:									
IBP	81	78	82	80	86	84	86	96	88
5	96	92	100	94	96	104	108	111	103
10	112	99	116	104	102	116	122	124	118
20	150	120	150	124	122	144	152	146	142
30	190	144	184	150	140	180	188	170	168
40	210	170	210	182	162	206	212	192	198
50	220	194	228	220	188	220	232	220	216
60	246	215	252	232	210	236	254	243	238
70	274	232	272	282	240	240	270	268	264
80	304	252	300	318	272	276	310	294	292
90	362	290	338	340	312	316	338	340	328
95	384	338	360	376	356	358	382	356	368
EP	410	370	398	406	394	386	412	386	420
% Recovery	95.5	98.0	95.0	97.0	96.0	97.0	97.0	98.0	98.0
% Residue	0.6	0.6	0.4	0.6	1.0	0.6	0.6	1.0	0.6
% Loss	3.9	1.4	4.6	2.4	3.0	2.4	2.4	1.0	1.4
RON	99.9	99.6	99.4	99.1	100.2	99.6	99.6	100.0	99.6
MON	92.4	90.6	91.5	92.2	91.1	85.9	91.9	90.6	90.9
RVP	13.1	14.9	13.0	12.9	14.1	12.5	11.3	9.2	11.4
FIA:									
% Saturates	65.9	72.7	69.4	64.8	64.2	49.2	64.5	57.2	66.0
% Olefins	4.4	9.9	2.6	3.0	14.8	8.4	5.0	6.0	6.4
% Aromatics	29.7	17.4	28.0	32.2	21.0	42.4	30.5	36.8	27.6
Stated RON	100	100	100	100	100	100	100	100	100
Stated Lead Content (cc/gal)	3	3	3	3	3	0	3	3	3
Source*	D	D	D	N	N	N	L	L	L

*D = Detroit N = New Jersey L = Los Angeles

TABLE 60

PHYSICAL ANALYSES OF GASOLINE SAMPLES

	22	23	24	25	26	27	28	29	30
API Gravity	61.9	59.1	60.0	60.3	54.9	60.8	62.5	67.5	60.0
Distillation:									
IBP	86	92	102	90	99	92	84	94	106
5	98	106	122	101	118	110	108	110	118
10	110	116	138	132	134	126	110	118	134
20	126	132	160	158	163	146	132	134	154
30	148	150	176	184	196	172	160	150	175
40	170	168	204	203	224	194	190	177	192
50	196	199	222	222	252	216	212	200	216
60	222	218	240	238	280	236	236	216	236
70	252	250	260	256	290	256	260	236	252
80	290	280	288	278	304	294	292	260	283
90	348	310	328	310	359	328	342	300	314
95	378	340	342	346	382	366	370	335	340
EP	398	389	390	388	408	400	400	368	394
% Recovery	95.0	98.5	95.0	98.0	95.0	96.0	96.0	95.5	99.0
% Residue	0.8	0.8	0.6	0.5	1.0	0.5	0.4	0.6	0.5
% Loss	4.2	0.7	4.4	1.5	4.0	3.5	3.6	3.9	0.5
RON	95.3	92.1	88.4	90.4	91.8	88.4	89.9	90.3	89.8
MON	84.1	82.9	80.6	84.2	83.2	80.6	83.7	82.8	81.1
RVP	12.8	10.0	9.6	10.1	9.7	10.4	12.0	10.1	7.5
FIA:									
% Saturates	54.0	64.0	67.9	70.1	63.7	67.9	75.5	75.4	66.2
% Olefins	16.6	8.1	7.5	7.5	3.0	7.5	2.1	12.6	7.9
% Aromatics	29.4	27.9	24.6	22.4	33.3	24.6	22.4	12.0	25.9
State RON	94	94	91	91	91	91	91	91	91
Stated Lead Content (cc/gal)	0.5	0.5	0.5	0.5	0.5	0	0	0	0
Source*	N	L	D	N	L	D	D	N	L

*D = Detroit   N = New Jersey   L = Los Angeles

TABLE 61

CHEMICAL ANALYSIS OF GASOLINE SAMPLES

Fuel No.	Parts per Million (Wt.)											g/gal	Parts per Million (Wt.)					Percent	
	Fe	Ni	Cu	Al	Ca	Mg	Mn	Cr	Sn	Zn	Ti	Pb	Cl	Br	P	S	HCHO	C	H
1	<0.5	<0.5	<0.1	<0.5	<0.5	<2	<0.2	<0.5	<0.5	<2	<0.5	3.6	.040	.049	0.3	1100	2.7	85.2	13.8
2	"	"	"	"	"	"	"	"	"	"	"	3.0	.035	.040	0.1	215	1.9	84.6	14.2
3	"	"	"	"	"	"	"	"	"	"	"	1.9	.021	.003	5.2	380	3.3	85.1	13.7
4	"	"	"	"	"	"	"	"	"	"	"	2.7	.032	.037	2.0	205	3.6	84.5	13.7
5	"	"	"	"	"	"	"	"	"	"	"	2.25	.026	.028	5.3	180	1.4	85.1	14.2
6	"	"	"	"	"	"	"	"	"	"	"	1.3	.015	.016	0.4	195	7.3	85.0	13.8
7	"	"	"	"	"	"	"	"	"	"	"	2.4	.030	.032	0.6	320	3.8	85.3	14.3
8	"	"	"	"	"	"	"	"	"	"	"	2.1	.027	.027	0.2	130	1.4	85.4	14.0
9	"	"	"	"	"	"	"	"	"	"	"	1.6	.028	.002	0.2	710	2.5	86.1	13.8
10	"	"	"	"	"	"	"	"	"	"	"	0.8	.008	.012	0.3	500	4.4	85.6	13.5
11	"	"	"	"	"	"	"	"	"	"	"	2.5	.031	.034	1.2	715	2.6	85.0	13.8
12	"	"	"	"	"	"	"	"	"	"	"	1.9	.023	.026	6.9	410	1.3	84.3	13.9
13	"	"	"	"	"	"	"	"	"	"	"	2.4	.030	.029	6.4	170	13.0	85.3	13.7
14	"	"	"	"	0.6	"	"	"	"	"	"	3.0	.033	.039	0.2	240	12.0	84.7	14.3
15	"	"	"	"	0.8	"	"	"	"	"	"	2.6	.033	.034	10.2	60	3.9	84.7	13.3
16	1.0	"	"	"	<0.5	"	"	"	"	"	"	3.1	.038	.041	14.0	40	6.1	85.7	13.6
17	<0.5	"	"	"	0.7	"	"	"	"	"	"	2.6	.030	.033	0.1	55	16.0	84.9	13.8
18	"	"	"	"	<0.5	"	"	"	"	"	"	-	<.002	<.001	3.6	95	3.3	86.8	12.9
19	"	"	"	"	"	"	"	"	"	"	"	3.5	.058	.012	0.3	520	9.5	85.6	13.5
20	"	"	"	"	<0.8	"	"	"	"	"	"	3.0	.039	.045	0.1	440	9.9	86.4	12.7
21	"	"	"	"	<0.5	"	"	"	"	"	"	2.3	.026	.033	5.2	440	11.0	85.7	13.3
22	"	"	"	"	"	"	"	"	"	"	"	.6	.007	.007	0.1	100	16.0	85.4	13.2
23	0.5	"	"	"	0.5	3	"	"	"	"	"	.57	.007	.007	0.1	580	8.8	86.1	13.6
24	0.8	"	"	"	<0.5	<2	"	"	"	"	"	.6	.007	.008	0.4	12	5.1	86.2	13.6
25	<0.5	"	"	"	"	"	"	"	"	"	"	.57	.006	.007	0.1	115	2.4	85.8	13.7
26	"	"	"	"	"	"	"	"	"	"	"	.6	.007	.008	0.1	205	3.1	86.7	13.2
27	"	"	"	"	"	"	"	"	"	"	"	-	<.002	<.001	17.2	425	22.0	85.7	13.9
28	"	"	"	"	"	"	"	"	"	"	"	.26	.003	.024	12.6	130	11.0	86.0	13.9
29	0.5	"	"	"	0.9	"	0.3	"	"	"	"	-	<.002	<.001	22.8	100	16.0	84.2	14.3
30	0.5	"	"	"	<0.5	"	<0.2	"	"	"	"	-	<.002	<.001	0.2	760	34.0	86.1	13.8

TABLE 62

EFFECT OF DILUTION VARIABLE ON PARTICULATE MASS EMISSION RATES

NON-LEADED FUEL

						Particulate Collected (gm/mile)				Dilution Tube Thermal Profile (°F)				
Chassis Dyno Test Mode	Run No.	Dilution Tube Flow Rate (cfm)	Heat Exchanger in Dilution Tube (°F Drop)	Radiator at Air Intake	Dilution Tube (<40°F)	Andersen Sampler	Millipore Filter	Andersen + Millipore	Fiber Glass 1 cfm (avg. of 2)	Exhaust	Dilution Air	Sample Zone	Temperature of 1 cfm Filter	Dew Point
60 mph	164A	350	-	-	-	.0024	.0071	.0095	.0046	518	65	155	115	82
SS	169B	500	-	-	-	.0025	.0060	.0086	.0116	518	75	120	100	66
	152B	350	Air-5°F	-	-	.0017	.0012	.0029	.0055	500	80	140	103	77
	153B	350	H_2O-10°F	-	-	.0015	.0074	.0089	.0055	500	75	125	100	77
	154B	500	H_2O-25°F	-	-	.0026	.0079	.0105	.0075	482	85	121	98	65
	157B	350	-	Yes	-	.0021	.0131	.0152	.0057	500	60	124	100	76
	159B	500	-	Yes	-	.0023	.0182	.0205	.0066	525	55	110	92	67
	172B	350	-	-	Yes	.0029	.0062	.0091	.0096	530	38	145	110	78
LA-4	164C	350	-	-	-	.0466	.1073	.1539	.0793	300	85	90	85	
23 min	169C	500	-	-	-	.1133	.0333	.1466	.0466	302	80	85	80	
CS	152A	350	Air-5°F	-	-	.0886	.0280	.1166	.0466	302	80	95	80	
	153A	350	H_2O-10°F	-	-	.0746	.0373	.1119	.0303	302	75	80	77	
	154A	500	H_2O-25°F	-	-	.0733	.0933	.1666	.0533	300	85	80	75	
	157C	350	-	Yes	-	.0606	.1120	.1726	.0466	302	55	75	70	
	159C	500	-	Yes	-	.1000	.0666	.1666	.0533	302	60	75	72	
	172C	350	-	-	Yes	.0653	.0746	.1399	.0770	302	32	75	68	
Mod.	164B	350	-	-	-	.0243	.0882	.1125	.0365	302	85	90	83	
LA-4	169A	500	-	-	-	.0869	.0304	.1173	.0347	302	75	85	80	
41 min	157A	350	-	Yes	-	.0365	.0973	.1338	.0395	300	58	75	72	
CS	159A	500	-	Yes	-	.0608	.0913	.1521	.0652	302	60	75	70	
	172A	350	-	-	Yes	.0578	.0608	.1186	.0700	300	30	70	68	

TABLE 63

EFFECT OF DILUTION VARIABLE ON PARTICULATE MASS EMISSION RATES

0.5 LEADED FUEL

						Particulate Collected (gm/mile)				Dilution Tube Thermal Profile (°F)				
Chassis Dyno Test Mode	Run No.	Dilution Tube Flow Rate (cfm)	Heat Exchanger in Dilution Tube (°F Drop)	Radiator at Air Intake	Dilution Tube (<40°F)	Andersen Sampler	Millipore Filter	Andersen + Millipore	Fiber Glass 1 cfm (avg. of 2)	Exhaust	Dilution Air	Sample Zone	Temperature of 1 cfm Filter	Dew Point
60 mph	127B	350	-	-	-	.0026	.0213	.0239	.0166	482	65	135	99	64
SS	118B	500	-	-	-	.0154	.0191	.0345	.0212	464	85	130	104	68
	149B	350	Air-5°F	-	-	.0030	.0213	.0243	.0189	518	75	145	108	80
	144B	350	H_2O-20°F	-	-	.0058	.0305	.0363	.0214	554	70	139	108	79
	148B	500	H_2O-15°F	-	-	.0055	.0245	.0300	.0208	518	95	128	103	76
	133B	350	-	Yes	-	.0064	.0286	.0350	.0221	464	52	114	89	68
	137B	500	-	Yes	-	.0108	.0345	.0454	.0229	472	52	103	88	54
	174C	350	-	-	Yes	.0034	.0186	.0220	.0138	644	36	180	135	85
LA-4	127A	350	-	-	-	.1680	.2660	.4340	.1120	302	65	100	95	
23 min	118C	500	-	-	-	.2200	.1533	.3733	.1266	305	85	95	80	
CS	149A	350	Air-5°F	-	-	.1400	.0513	.1913	.0420	305	75	95	75	
	144A	350	H_2O-20°F	-	-	.1726	.0840	.2566	.0630	290	70	75	75	
	148A	500	H_2O-15°F	-	-	.2000	.0333	.2333	.0533	305	83	78	75	
	133C	350	-	Yes	-	.2426	.2380	.4806	.1446	300	52	78	70	
	137C	500	-	Yes	-	.3400	.2600	.6000	.1133	302	52	75	68	
	174A	350	-	-	Yes	.0793	.0933	.1726	.1166	300	37	75	75	
Mod.	124A	350	-	-	-	.0761	.1025	.1796	.0517	305	60	105	88	
LA-4	118A	500	-	-	-	.0652	.1174	.1826	.1130	302	78	95	82	
41 min	133A	350	-	Yes	-	.1552	.1735	.3286	.0608	305	52	75	72	
CS	137A	500	-	Yes	-	.0739	.1782	.2521	.0391	302	52	75	70	
	174B	350	-	-	Yes	.0793	.0933	.1726	.1166	300	37	70	70	

TABLE 64

LEAD AND BENZO-α-PYRENE ANALYSIS

0.5 LEADED FUEL

Chassis Dyno Test Mode	Run No.	Dilution Tube Flow Rate (cfm)	Heat Exchgr. in Dilution Tube (°F Drop)	Radiator at Air Intake	Dilution Air (<40°F)	Wt. Percent Lead by Atomic Absorption on Andersen Plate No.			BaP ppm Based on Total Particulate*
						1 + 2	3 + 4	5 + 6	
60 mph	127B	350	-	-	-	3.00	3.12	3.62	30
SS	118B	500	-	-	-	0.27	0.08	0.35	280
	149B	350	Air-5°F	-	-	1.33	1.50	2.83	90
	144B	350	H_2O-20°F	-	-	0.56	0.38	2.43	15
	148B	500	H_2O-15°F	-	-	0.53	0.53	1.66	85
	133B	350	-	Yes	-	2.40	2.18	2.09	80
	137B	500	-	Yes	-	0.42	0.19	0.85	105
	174C	350	-	-	Yes	0.35	0.40	1.00	60
LA-4	127A	350	-	-	-	0.69	1.00	0.75	440
23 min	118C	500	-	-	-	0.82	0.76	0.79	30
CS	149A	350	Air-5°F	-	-	0.97	1.00	1.77	35
	144A	350	H_2O-20°F	-	-	0.62	0.54	0.30	345
	148A	500	H_2O-15°F	-	-	0.00	0.00	0.10	160
	133C	350	-	Yes	-	-	-	-	95
	137C	500	-	Yes	-	0.75	0.92	0.71	60
	174A	350	-	-	-	1.06	2.86	1.20	60
Mod.	124A	350	-	-	-	0.88	0.60	0.92	90
LA-4	118A	500	-	-	-	1.60	1.93	1.46	1025
41 min	133A	350	-	Yes	-	0.24	0.22	0.19	345
CS	174B	350	-	-	Yes	1.05	1.05	0.94	120

*From 1 cfm filter

TABLE 65
BENZO-α-PYRENE ANALYSIS
NON-LEADED FUEL

Chassis Dyno Test Mode	Run No.	Dilution Tube Flow Rate (cfm)	Heat Exchgr. in Dilution Tube (°F Drop)	Radiator at Air Intake	Dilution Air (<40°F)	BaP ppm Based on Total Particulate* Mass
60 mph	164A	350	-	-	-	170
SS	169B	500	-	-	-	30
	152B	350	Air-5°F	-	-	15
	153B	350	H_2O-10°F	-	-	115
	154B	500	H_2O-25°F	-	-	95
	157B	350	-	Yes	-	165
	159B	500	-	Yes	-	60
	172B	350	-	-	Yes	5
LA-4	164C	350	-	-	-	215
23 min	169C	500	-	-	-	85
CS	152A	350	Air-5°F	-	-	10
	153A	350	H_2O-10°F	-	-	50
	154A	500	H_2O-25°F	-	-	120
	157C	350	-	Yes	-	85
	159C	500	-	Yes	-	105
	172C	350	-	-	Yes	85
Mod.	164B	350	-	-	-	170
LA-4	169A	500	-	-	-	185
41 min	157A	350	-	Yes	-	270
CS	159A	500	-	Yes	-	295
	172A	350	-	-	Yes	530

*From 1 cfm filter

TABLE 66

PARTICULATE TRACE METAL ANALYSIS - MILLIPORE FILTER PAPERS - LEADED FUEL

Chassis dyno Test Mode	Run No.	Diln Tube Flow rate (cfm)	Heat Exch in Dl tube (°F drop)	Radiator at air inlet	Dilution air 40°F	Weight Percent											
						Fe	Ni	Cu	Al	Ca	Mg	Mn	Cr	Si	Zn	Ti	Pb*
60 MPH S.S.	127b	350	-	-	-	.108	<.027	.095	.041	.77	.162	<.014	<.014	<.014	<.081	<.014	13.1
	118b	500	-	-	-	.13	<.04	.13	.065	1.54	.30	<.02	<.04	<.04	.15	<.04	12.78
	149b	350	Air-5°F	-	-	.02	.011	.047	.02	.376	<.035	<.005	<.012	<.012	<.035	<.012	15.4
	144b	350	H_2O-20°F	-	-	.034	<.01	.05	.04	.425	.059	<.004	.01	<.01	.05	<.01	19.8
	148b	500	H_2O-15°F	-	-	.03	<.015	.076	.045	.80	.106	<.10	.015	<.015	.06	<.015	15.4
	133b	350	-	Yes	-	.04	<.02	.061	.031	.408	.091	<.01	<.02	<.02	.07	<.02	13.57
	137b	500	-	Yes	-	.072	<.024	.108	.036	.75	.132	<.012	<.024	<.072	<.024	<.024	9.18
	174c	350	-	-	Yes	.31	<.013	.11	.064	.59	.16	<.013	.013	.012	.27	<.013	29.0
LA-4 23 min cold start	127a	350	-	-	-	.42	<.035	.158	.21	2.31	.386	<.017	<.035	<.035	<.105	<.035	7.4
	118c	500	-	-	-	.74	<.086	.26	.13	3.08	.56	<.04	<.08	<.08	<.26	<.08	4.87
	149a	350	Air-5°F	-	-	.182	.091	.223	.182	3.82	.364	<.045	<.091	<.091	<.27	<.091	30.6
	144a	350	H_2O-20°F	-	-	.222	.056	.28	.167	2.89	.28	<.028	.056	<.056	<.167	<.056	13.2
	148a	500	H_2O-15°F	-	-	1.2	<.20	1.0	.60	9.80	.80	<.10	<.20	<.20	<.60	<.20	14.1
	133c	350	-	Yes	-	.157	<.04	.176	.08	1.19	.235	<.02	<.02	<.02	<.117	<.02	26.9
	137c	500	-	Yes	-	.103	<.051	.154	.051	.949	.21	<.026	<.051	<.051	<.154	<.051	15.29
	174a	350	-	-	Yes	1.30	.27	.59	.16	1.70	.38	<.05	<.05	<.05	.77	<.05	8.9
Modified LA-4 41 minute cold start	124a	350	-	-	-	.235	<.058	.088	<.058	1.32	.294	<.029	<.058	<.058	<.176	<.058	13.2
	118a	500	-	-	-	.222	<.07	1.44	.148	2.29	.48	<.037	<.07	<.07	<.22	<.07	8.88
	133a	350	-	Yes	-	.14	<.035	.158	.05	1.10	.193	<.017	<.035	<.035	<.015	<.035	8.33
	137a	500	-	Yes	-	.146	<.049	.195	.073	1.05	.27	<.024	<.049	<.049	<.146	<.049	11.11
	174b	350	-	-	Yes	.38	<.04	.23	.12	1.70	.43	<.04	.048	<.04	.16	<.04	5.4

* by Atomic Absorption Analysis

TABLE 67

TRACE METAL ANALYSIS - MILLIPORE FILTER PAPERS

NON-LEADED FUEL

Chassis Dyno Test Mode	Run No.	Dilution Tube Flow Rate (cfm)	Heat Exchanger in Dilution Tube (°F Drop)	Radiator at Air Intake	Dilution Air (<40°F)	Weight Percent											
						Fe	Ni	Cu	Al	Ca	Mg	Mn	Cr	Sn	Zn	Ti	Pb*
60 mph	164A	350	-	-	-	.31	.03	.31	.14	3.00	.35	.017	.03	.03	.10	.03	1.4
SS	169B	500	-	-	-	.25	.06	.31	.25	4.56	.56	.03	.06	.06	.187	.06	11.3
	152B	350	Air-5°F	-	-	.6	.20	1.0	.6	11.2	1.4	.10	.20	.20	1.0	.6	11.5
	153B	350	H_2O-10°F	-	-	.107	.036	.178	.07	2.11	.214	.10	.036	.036	.107	.036	1.0
	154B	500	H_2O-25°F	-	-	.143	.048	.286	.095	2.86	.286	.024	.048	.048	.143	.048	1.8
	157B	350	-	Yes	-	.04	.02	.08	.06	.92	.10	.01	.02	.02	.06	.02	.1
	159B	500	-	Yes	-	.11	.02	.11	.06	1.32	.13	.01	.02	.02	.06	.02	.2
	172B	350	-	-	Yes	.23	.038	.19	.15	2.57	.27	.019	.038	.038	.115	.038	18.9
LA-4	164C	350	-	-	-	.167	.042	.25	.13	2.88	.29	.02	.042	.042	.12	.042	.7
23 min	169C	500	-	-	-	.8	.20	.8	.6	14.2	1.2	.10	.20	.20	.60	.20	17.1
CS	152A	350	Air-5°F	-	-	.5	.167	.83	.5	8.33	1.0	.083	.167	.167	.5	.167	1.3
	153A	350	H_2O-10°F	-	-	.222	.111	.555	.222	7.00	.67	.056	.111	.111	.333	.036	.4
	154A	500	H_2O-25°F	-	-	.21	.07	.28	.14	3.71	.42	.035	.07	.07	.21	.07	2.5
	157C	350	-	Yes	-	.125	.04	.16	.08	2.29	.25	.02	.04	.04	.125	.04	1.7
	159C	500	-	Yes	-	.40	.10	.50	.30	7.0	.70	.05	.10	.10	.30	.10	1.4
	172C	350	-	-	Yes	.31	.06	.25	.188	4.94	.56	.03	.06	.06	.188	.06	15.0
Mod.	164B	350	-	-	-	.21	.03	.24	.10	2.76	.276	.017	.03	.03	.10	.03	2.7
41 min	169A	500	-	-	-	.71	.14	1.14	.86	12.43	1.28	.07	.143	.143	.43	.143	7.2
CS	157A	350	-	Yes	-	.094	.031	.125	.063	1.78	.156	.015	.031	.031	.094	.031	1.0
	159A	500	-	Yes	-	.14	.048	.14	.096	2.05	.19	.024	.048	.048	.14	.048	1.4
	172A	350	-	-	Yes	.30	.05	.20	.15	3.65	.35	.025	.05	.05	.15	.05	7.6

*by Atomic Absorption

C. EVALUATION OF BETA-GAUGE

Tables 68, 69, and 70 present mass emission data for exhaust particulate matter as measured by the Industrial Nucleonics Beta-gauge and conventional proportional filtering devices.

TABLE 68

EVALUATION OF INDUSTRIAL NUCLEONICS BETA GAUGE

Test Vehicle: 1971 Chevrolet - 350 CID V8 Engine

Test Fuel: A (2.66 TEL/gallon)

Run No.	Driving Condition	Sampling Time (min)	Beta Mass Gain (μ gm)	Integrated Flow (liters)	142 mm Filter Wgt. Gain (mg)	Avg. Beta Flow Rate (l/min)	Beta Emission Rate (mg/min)	142 mm Emission Rate (mg/min)	Deviation Beta vs. 142 mm (%)	Notes
2	30 mph SS	20	2980	2135	3.65	104.2	18.21	22.8	-20.1	A,B
3	30 mph SS	20	2491	1935	3.85	87.1	18.22	24.1	-24.2	A,B
4	30 mph SS	20	2485	1840	3.60	82.8	19.11	22.5	-15.1	A,B
5	60 mph SS	20	Abort							C
6	60 mph SS	20	2366	874	13.2	41.4	38.31	82.5	-53.6	A,B
7	LA-4 CS	23	3230	1022	14.0	41.1	34.4	76.1	-54.8	A,B
8	LA-4 HS	10	2151	787	4.05	72.9	41.7	50.6	-17.8	A,B
9,10	LA-4 HS	23	Abort							C
11	60 mph SS	10	3627	453	9.15	45.3	113.3	114.4	-1.0	D
12	60 mph SS	10	3870	795	5.80	79.5	68.9	72.5	-5.0	D
13	60 mph SS	10	1929	417	5.75	41.7	65.4	71.9	-8.9	D
14	30 mph SS	15	1502	1184	2.40	78.9	18.0	20.0	-10.3	D
15	15 mph SS	15	1437	1382	1.75	92.1	14.7	14.8	-0.6	D

Notes: A - Swirlmeter downstream of pump; standing wave in flow meter causing error in flow measurement

B - Average flow rate corrected for elevated pump exhaust temperature

C - Test aborted due to computer cycling malfunction

D - Swirlmeter relocated to inlet upstream of filter; temperature correction not required

TABLE 69

EVALUATION OF INDUSTRIAL NUCLEONICS BETA GAUGE

Test Vehicle: 1971 Chevrolet - 350 CID V8 Engine   Test Fuel: 0.5 cc TEL/gallon, 91 RON

Run	Driving Condition	Sampling Time (min)	Beta Mass Gain (μgm)	Integrated Flow (liters)	Filter Wt. Gain (mg)		Avg. Beta Flow (1/min)	Emission Rate (mg/min)			Deviation (%)			Notes
					142 mm	47 mm		Beta	142 mm	47 mm	β-142 mm	β-47 mm	47 mm-142 mm	
22	LA-4 CS	23	2796	1784	7.1	8.2	77.6	22.1	38.6	54.2	-42.4	-59.0	54.1	D,E,J
23	LA-4 HS	10	960	1222	1.6	0.9	122.2	11.1	20.0	13.7	-44.0	-18.7	-31.7	D,E
24	LA-4 HS	23	251	506	2.3	1.3	22.0	7.0	12.5	8.6	-43.0	-18.4	-31.3	D,E,H
25	LA-4 HS	23	298	506	2.4	1.4	22.0	8.3	13.0	9.3	-36.3	-10.3	-29.1	D,E,F,H
26	LA-4 HS	23	959	1840	2.5	1.4	80.0	7.4	13.6	9.3	-45.7	-20.3	-31.9	D,E
27	60 mph SS	15	4119	993	7.0	4.6	66.2	58.7	70.9	52.5	-17.2	12.0	-26.0	D,E,G,J
28	30 mph SS	15	350	966	1.2	0.4	64.4	5.5	12.2	4.1	-58.0	26.0	-66.7	D,E,G
29	15 mph SS	15	332	1469	0.7	0.3	97.9	3.2	7.1	3.0	-55.0	5.0	-57.1	D,E,G
30	Idle	15	248	1488	0.5	0.2	99.2	2.4	5.1	2.0	-53.4	16.4	-60.0	D,E,G
31	30 mph SS	15	510	1472	1.5	0.5	98.1	4.9	12.5	5.2	-60.8	-3.2	-59.5	D,E
32	60 mph SS	5	2308	496	3.0	1.6	99.2	65.5	75.0	48.6	-12.7	34.6	-35.1	D,E
33	60 mph SS	5	1605	495	2.2	1.2	99.0	45.7	55.0	36.5	-16.8	25.4	-33.7	D,E

Notes: D - Swirlmeter relocated in inlet (upstream of filter)
E - 47 mm parallel filter used in addition to 142 mm filter (47 mm flow = 3.29 cfm)
F - Gelman Type A filter used in cassette
G - Flow through parallel filters identical (3.29 cfm)
H - Face velocity through 47 mm and cassette equal
J - 47 mm filter plugged, ΔP excessive

Flow rate for 142 mm filter = 4 cfm except under footnote G.

TABLE 70

EVALUATION OF INDUSTRIAL NUCLEONICS BETA GAUGE

Test Vehicle: 1971 Chevrolet - 350 CID V8 Engine   Test Fuel: Indolene 0 (No lead)

Run	Driving Condition	Sampling Time (min)	Beta Mass Gain (μgm)	Integrated Flow (liters)	Filter Wt. Gain (mg)		Avg. Beta Flow (1/min)	Emission Rate (mg/min)			Deviation (%)			Notes
					142 mm	47 mm		Beta	142 mm	47 mm	β-142 mm	β-47 mm	47 mm-142 mm	
16	LA-4 CS	23	1049	2454	4.05	-	106.7	6.1	22.0	-	-72.5	-	-	D
17	LA-4 HS	10	156	1208	1.35	-	120.8	1.8	16.9	-	-89.1	-	-	D
18	LA-4 HS	23	33	736	1.4	-	32.0	0.64	7.6	-	-91.6	-	-	D
19	LA-4 HS	23	230	2075	1.40	-	90.2	1.6	7.6	-	-79.4	-	-	D
20	LA-4 HS	23	197	2378	1.40	0.2	103.4	1.2	7.6	1.3	-84.6	-11.3	-82.5	D,E
21	California	47.5	359	4750	2.20	0.6	100.0	1.1	5.8	1.9	-81.0	-43.8	-66.8	D,E,K

Notes: D - Swirlmeter relocated to inlet (upstream of filter)

E - 47 mm parallel filter used in addition to 142 mm filter

K - Test aborted because of brake failure on car

Flow rate for 142 mm filter = 4 cfm
Flow rate for 47 mm filter = 3.3 cfm (showed 6.5" Hg pressure differential)

IV. DISCUSSION OF RESULTS

A. EVALUATION OF DILUTION TUBE VARIABLES ON THE COLLECTION OF EXHAUST PARTICULATE MATTER

Prior to a discussion of the effects of dilution air flow rate and dilution air cooling on the observed mass emission rates of exhaust particulate matter, consideration will be given to the influence of fuel and vehicle operating sequence on this parameter.

The use of low-lead gasoline resulted in the emission of higher levels of exhaust particulate than were observed for non-leaded gasoline. This result was not unexpected and corroborates the similar finding in Phase I of this contract effort.

Of the three vehicle operating sequences employed, the two cold start cyclic sequences afforded higher particulate mass emission rates than did 60 mph steady state operation. This is to be expected, since during the early modes of the cold start test cycles, the vehicle is operating in a choked condition. Higher particulate mass emission rates were generally observed for the cold start 23 minute LA-4 cycle than for the 41 minute LA-4 sequence. This was again anticipated, since even though the actual collected mass of particulate generally increased with the longer cycle, the grams per mile declined because of the relatively shorter period of cold start operation. In order to prove that volatile organic particulate was not being lost from the filtering devices during the ten minute engine shut down period of the 41 minute cycle, an experiment was performed in which a 1 cfm glass fiber filter was exposed during the course of a 23 minute cold start LA-4 cycle. The filter was weighed upon completion of the test run and replaced in the system. Dilution air alone was passed through the filter at 1 cfm for ten minutes and the filter reweighed. No loss in weight was observed.

An examination of the relative weights of particulate matter collected on the plates of the Andersen impactor versus the back-up Millipore filter for the three vehicle modes studied, suggests that there is an overall increase in particle size as one moves from 60 mph steady state operation to the 41 minute cycle, and a further increase in size for the 23 minute LA-4 cycle. This is confirmed by an examination of the particulate mass distribution profiles shown in Appendix D. It is suggested that these data result from the relatively high concentrations of exhaust products which occur during the choked or partially choked conditions found in the early stages of the cold start cycle and from the relatively low temperatures present throughout the exhaust system and dilution tunnel during this same period. Such conditions would favor the formation or growth of large exhaust particulate matter.

In general, the concentrations of benzo-α-pyrene associated with the collected particulate matter were higher in the cyclic modes of vehicle operation. This again is believed to result from the relatively inefficient combustion which occurs during the early stages of a cold start test sequence.

Examination of the mass distribution profiles for leaded particulate matter collected during the test series performed with low lead fuel, indicates a general decrease in particle size when one compares steady state to cyclic operation.

A comparison of the efficiencies of the various collection devices employed in this phase of the program indicates that the Andersen sampler and back-up 142 mm Millipore filter, operated at 1 cfm, afforded higher levels of particulate matter than did a 142 mm glass fiber filter operating at the same flow rate. This observation corroborates the findings in Phase I of this contract effort.

Comparison of the particulate mass emission rates at dilution tube flow rates of 350 and 500 cfm shows no apparent trend in results. However, an examination of the relevant mass distribution profiles in Appendix D indicates an overall increase in particle size at the higher dilution tube flow rate. This conclusion is supported by analysis of the relative weights of particulate matter collected on the plates of the Andersen sampler versus the back-up Millipore filter. This increase in particle size is believed to result from entrainment of larger particles in the diluted exhaust stream at the higher dilution tube flow rate. Such particles might be expected to suffer gravitational fall out at lower diluent air velocities.

Increasing the dilution tube flow rate to 500 cfm afforded no significant trends in either the concentrations of lead or benzo-α-pyrene in the collected exhaust particulate. However, an increase in the trace metal content of the material on the Millipore filter was evident for both fuels studied.

Use of a water cooled automotive radiator ahead of the dilution tube air intake gave a temperature drop of 15-30°F for the diluent air. With this device in position, an increase in the mass emission rates for particulate matter was generally observed. Presumably this increase is the result of the condensation of organic matter accelerated by the lower temperatures of the dilution air. This hypothesis is supported by the observed increase in the particulate concentration of benzo-α-pyrene, and by a decrease in the concentration of trace metals associated with particulate collected on the Millipore filter. Cooling of the dilution air also resulted in the collection of particulate matter having a smaller MMED for non-leaded gasoline. No such effect was evident for low-leaded fuel.

The use of a water-cooled heat exchanger within the dilution tunnel generally afforded a reduction in the observed particulate mass emission rates. This was particularly pronounced during 23 minute LA-4 cold start cyclic operation. It should be noted that the temperature drop across the heat exchanger was only 15-25°F but that this was nevertheless sufficient to affect the measured emission rates for particulate matter. This decrease in observed particulate emissions is believed to result from condensation onto the surface of the heat exchanger. Physical trapping of particulate matter by direct impingement on the device should be minimal because of its design and mode of introduction into the dilution tube. The above trend was observed for both non-leaded and low lead fuels.

Examination of the relevant particulate mass distribution profiles indicates that use of the cooling coil under 60 mph steady state vehicle operating conditions resulted in a shift in the MMED of collected particulate matter to a smaller size for low lead fuel and to a larger size for non-leaded fuel. Under the operating conditions of the cold start 23 minute LA-4 cycle, the converse was true.

No significant trends are obvious for either the particulate concentrations of benzo-α-pyrene or trace metals as a function of diluted exhaust effluent cooling.

Throughout the above test program, filter temperature and dew point determinations (Tables 62 and 63) indicated that there was sufficient spread between these two sets of data to minimize problems associated with condensation of moisture on filter surfaces.

B. EVALUATION OF BETA-GAUGE PARTICULATE MASS MEASURING DEVICE

A study of the data collected during the evaluation of the Industrial Nucleonics particulate emission Beta-gauge indicates that there was close correlation between the mass emission rates measured by this device and via a 142 mm glass fiber filter, operated at 4 cfm, when the particulate matter was generated by a vehicle running under steady state conditions on gasoline containing 3 cc TEL/gallon. After initial operational problems with the device were corrected, the deviation between the mass emission rates measured above was from 0.6-10.3 percent. In all cases the conventional filter afforded the higher values (Table 68).

A similar series of tests were made on a vehicle operating on low-leaded fuel (0.5 cc TEL/gallon). Under the conditions of both hot and cold start 23 minute LA-4 cycles, the deviation between the Beta-gauge and 142 mm (4 cfm) filter ranged from 36.3-45.7 percent. The corresponding deviation between the Beta-gauge and the 47 mm filter (3.29 cfm) ranged from 10.3-18.7 percent. Again the conventional filters afforded the higher mass emission rates. Under steady state vehicle operation, the deviation in mass emission rates between the Beta-gauge and 142 mm filter ranged from 12.7 to 60.8 percent. The corresponding deviation between the 47 mm filter and Beta-gauge was 5-34 percent. However, in this latter instance, the Beta-gauge afforded the higher mass emission rates.

In a final set of experiments, the measuring capabilities of the Beta-gauge and conventional filters were compared using a vehicle running on non-leaded fuel. In a series of cyclic runs, there was considerable deviation (79-91 percent) between the mass emission rates afforded by the Beta-gauge and 142 mm filters.

Thus the ability of the Beta-gauge to correlate well with glass fiber filter measurements became less reliable as the level of tetraethyl lead in the test fuel was reduced. Two factors are believed to contribute to the observed discrepancies.

The face velocity of air diluted exhaust effluent through the filter membrane of the Beta-gauge was in general much higher than that through the regular filters. With non-leaded fuel specially, this could result in the more rapid volatilization of organic particulate from the filter medium, thus yielding a lower observed mass emission rate.

Further, although the glass fiber filters utilized are relatively insensitive to air-borne moisture, the Pallflex filter medium used in the Beta-gauge is more sensitive in this regard. Thus, this factor may also be responsible in part for the observed deviations.

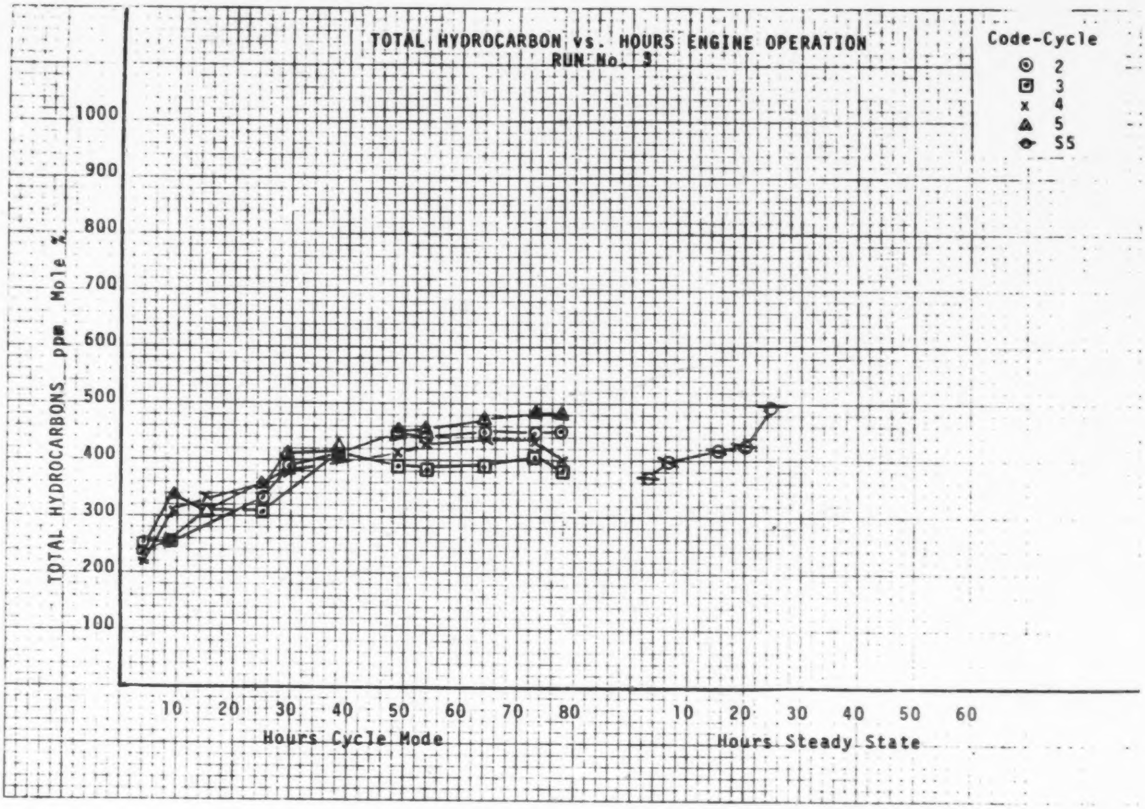
APPENDIX A

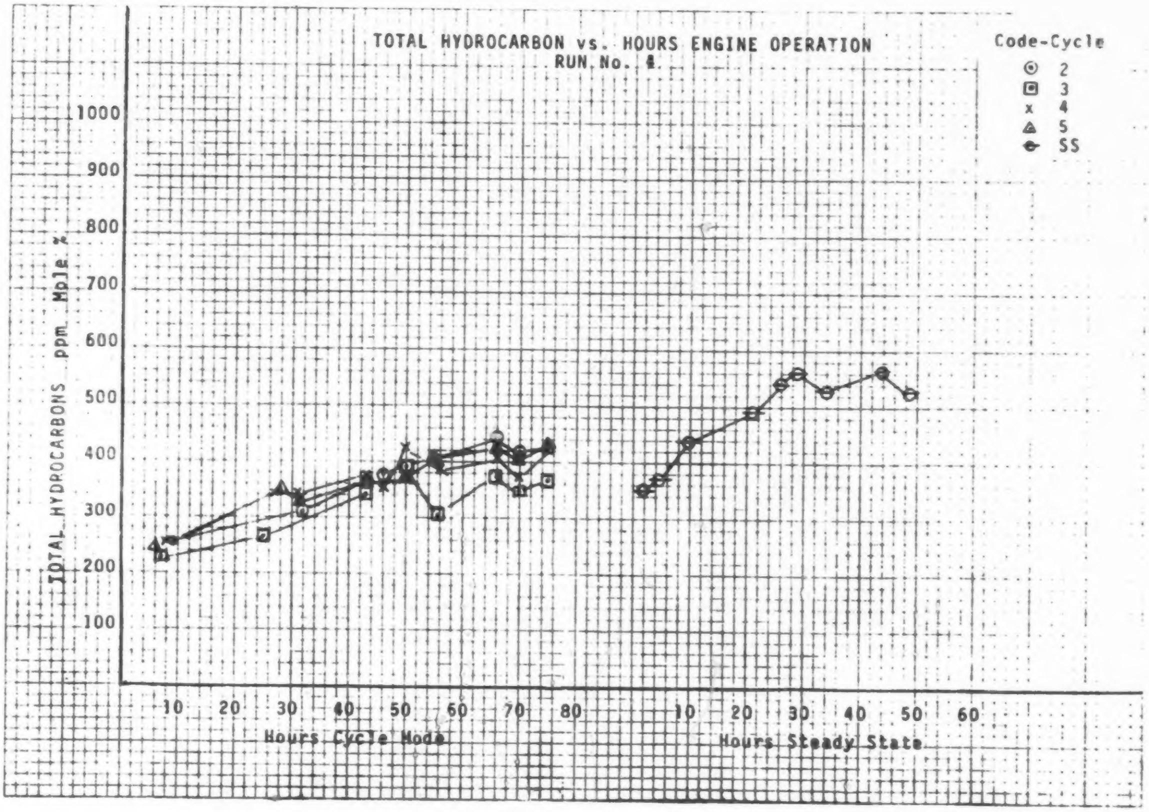
Total unburned hydrocarbon emissions (ppm Mole %) as a function of engine or vehicle operating hours for all test fuel runs. Vehicle emissions determined during cruise mode operation only (60 mph - road load).

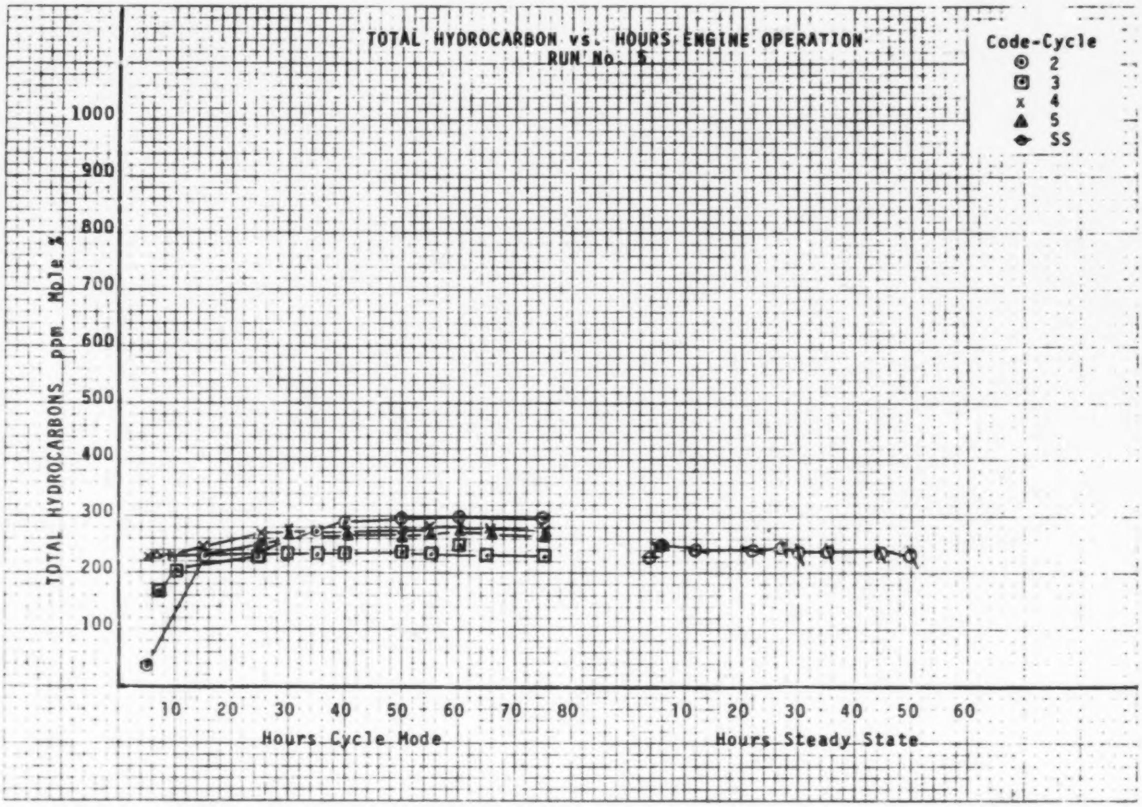
Legend:

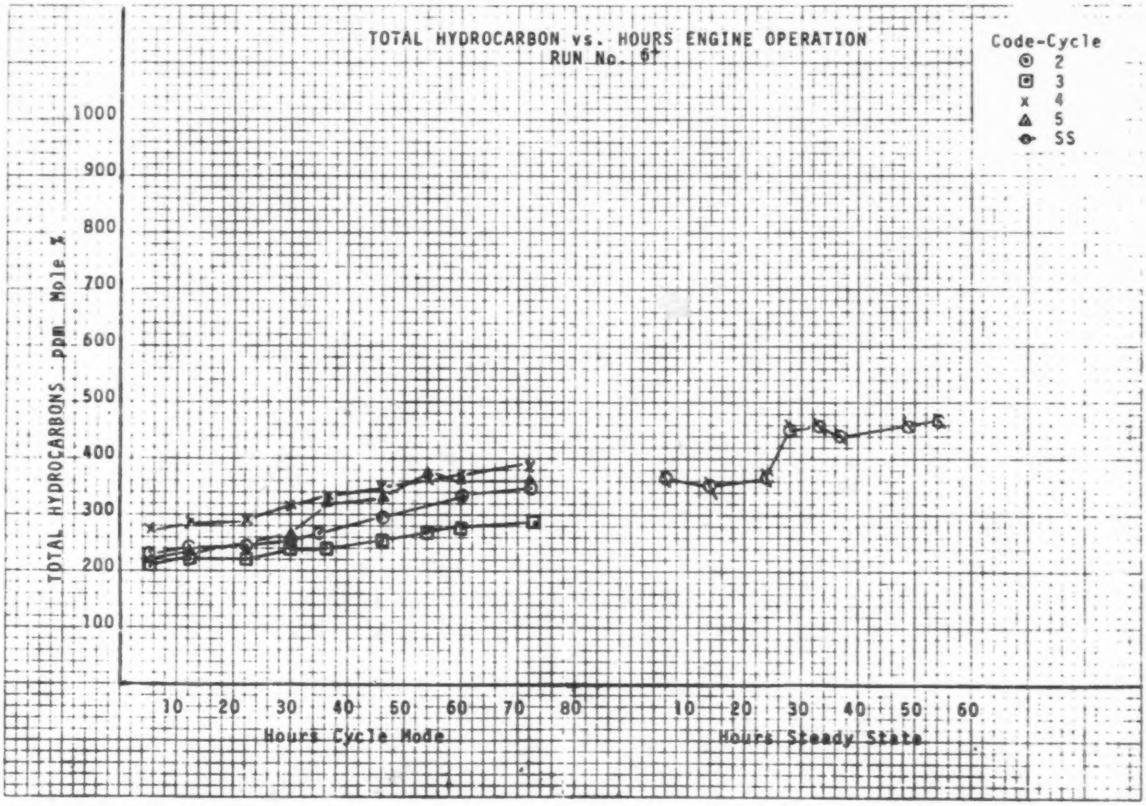
Code	Cycle No.*	
⊙	2	
⊡	3	
x	4	
◬	5	
-⊖-	SS	Steady State (cruise mode 60 mph road load)

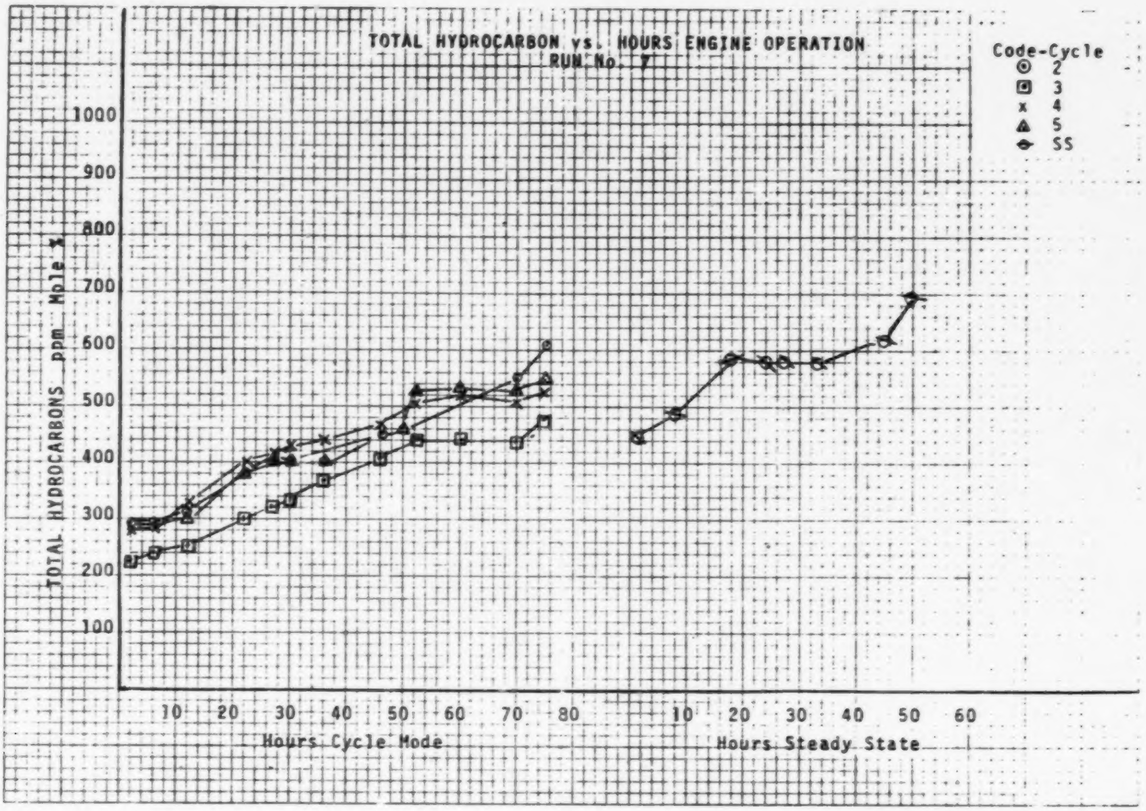
*See Table 2, page 13.

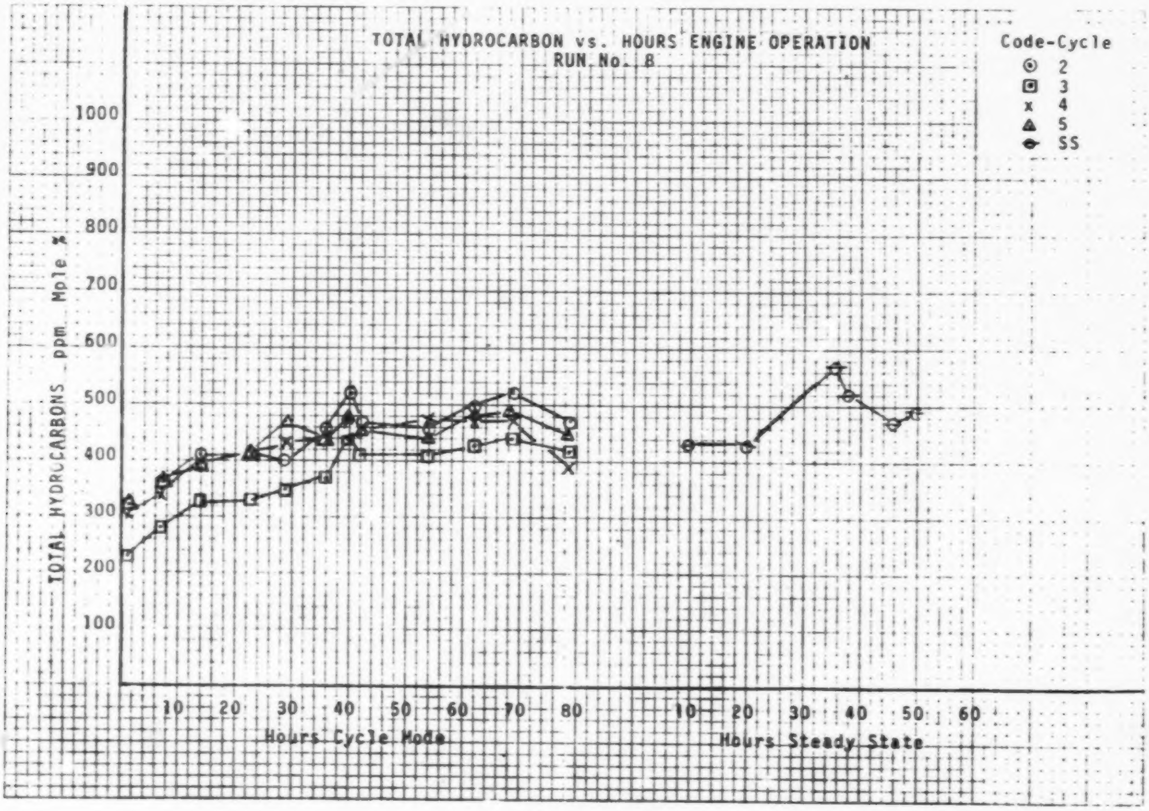

TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
RUN No. 3
Code-Cycle
⊙ 2
⊡ 3
x 4
▲ 5
⊖ SS
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
Hours Cycle Mode
10
20
30
40
50
60
Hours Steady State

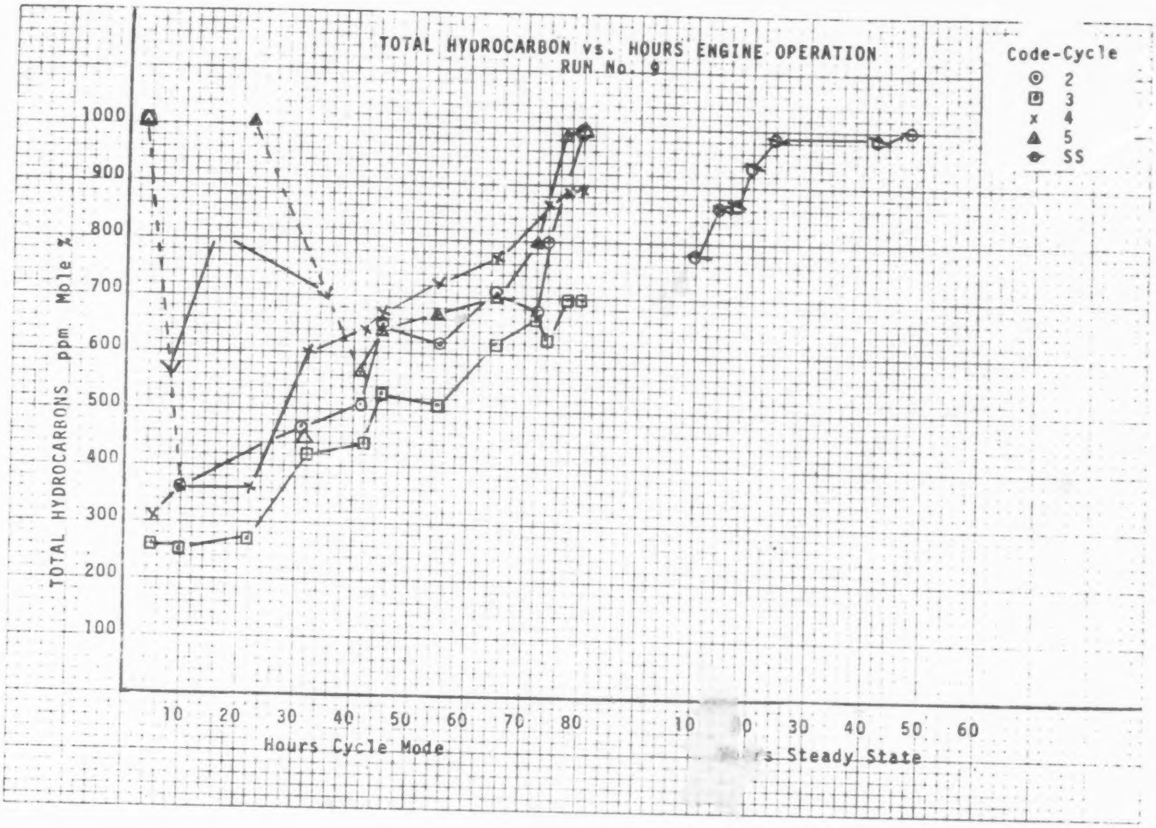

TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
RUN No. 4
Code-Cycle
⊙ 2
⊡ 3
x 4
△ 5
⊖ SS
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
Hours Cycle Mode
10
20
30
40
50
60
Hours Steady State

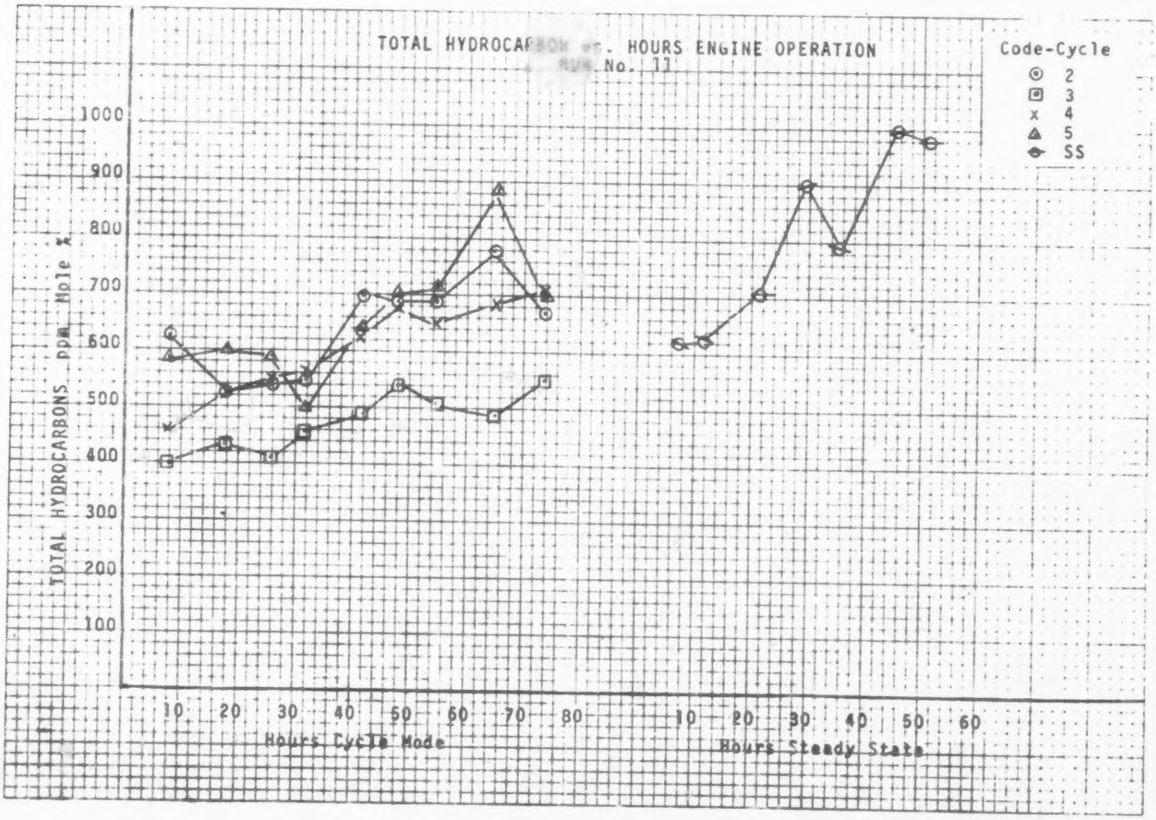

TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
RUN No. 5
Code-Cycle
⊙ 2
▣ 3
x 4
▲ 5
SS
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
Hours Cycle Mode
10
20
30
40
50
60
Hours Steady State

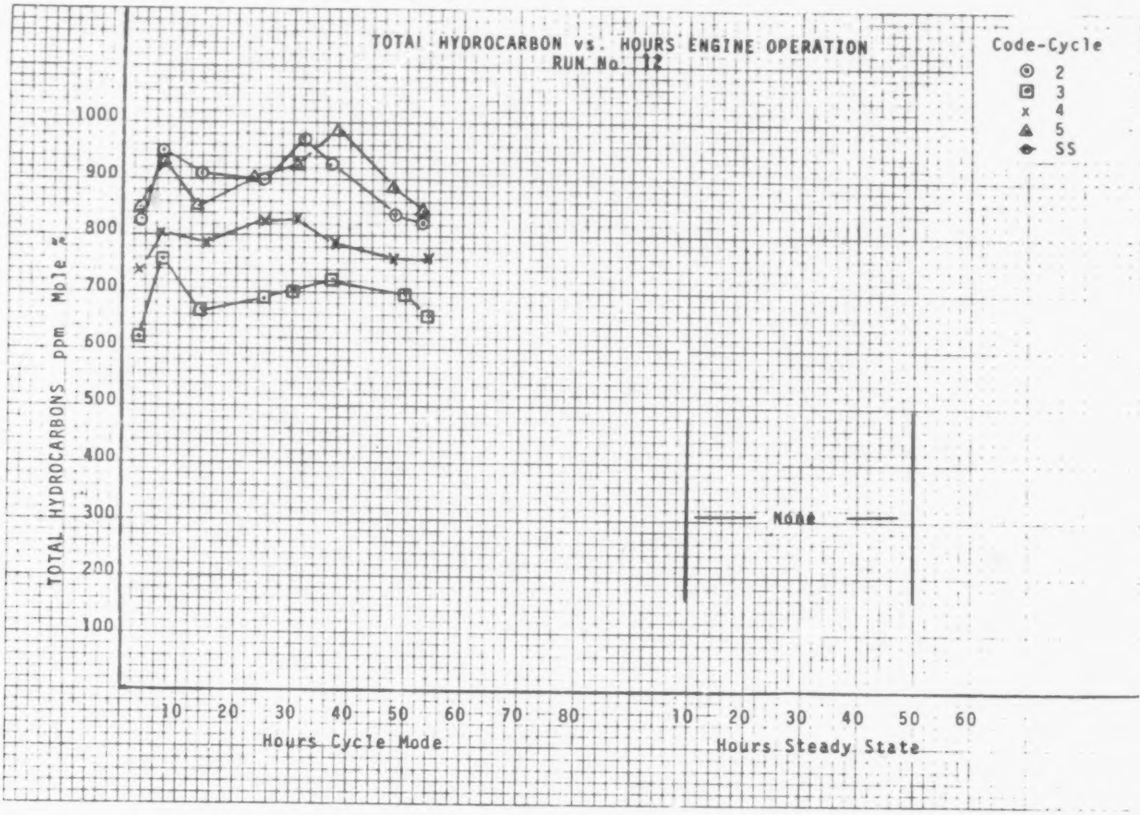

TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
RUN No. 6†
Code-Cycle
⊙ 2
▣ 3
x 4
△ 5
SS
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
Hours Cycle Mode
10
20
30
40
50
60
Hours Steady State

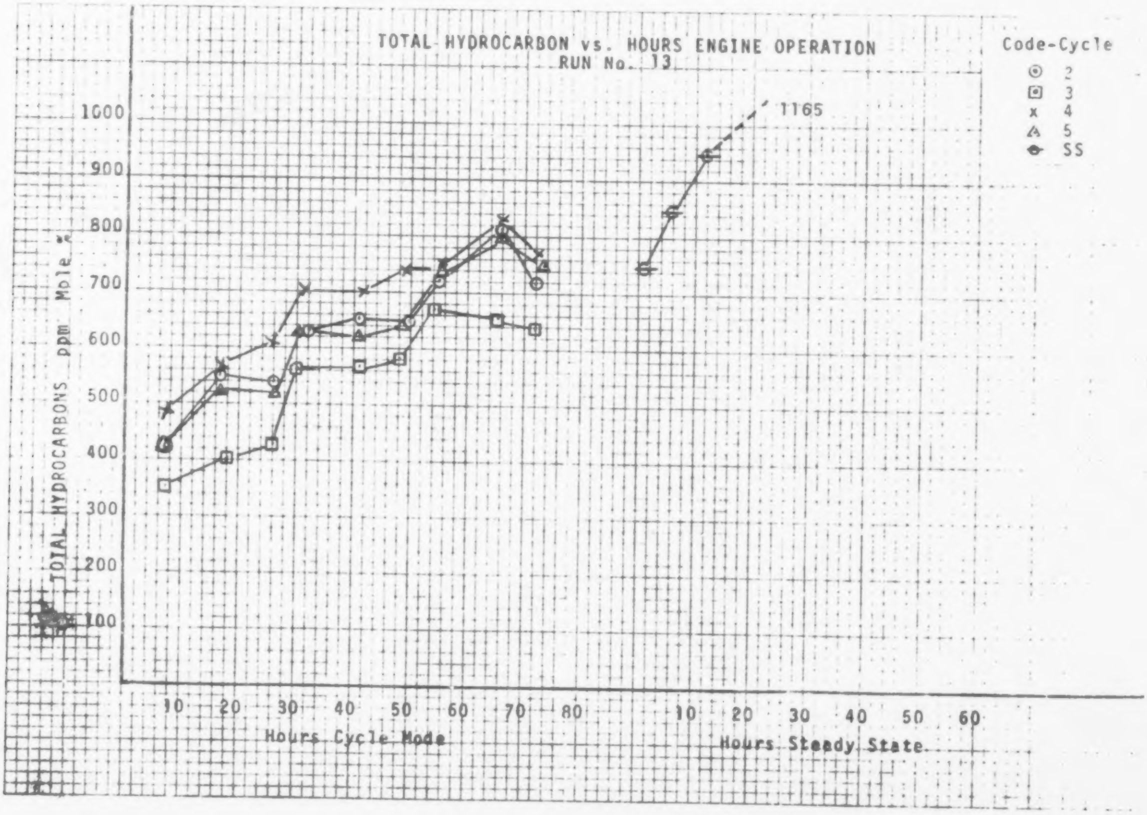

TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
RUN No. 7
Code-Cycle
⊙ 2
⊡ 3
x 4
▲ 5
-○- SS
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
Hours Cycle Mode
10
20
30
40
50
60
Hours Steady State

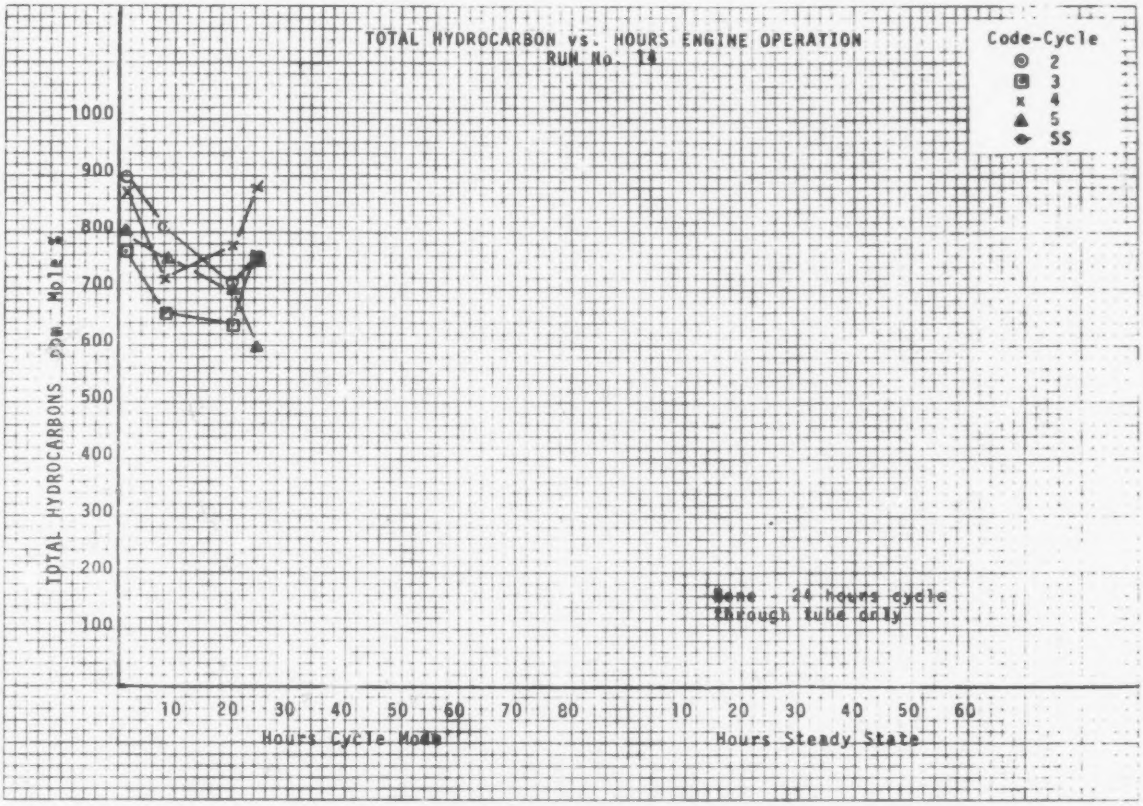

TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
RUN No. 8
Code-Cycle
⊙ 2
⊡ 3
x 4
▲ 5
-○- SS
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
Hours Cycle Mode
10
20
30
40
50
60
Hours Steady State

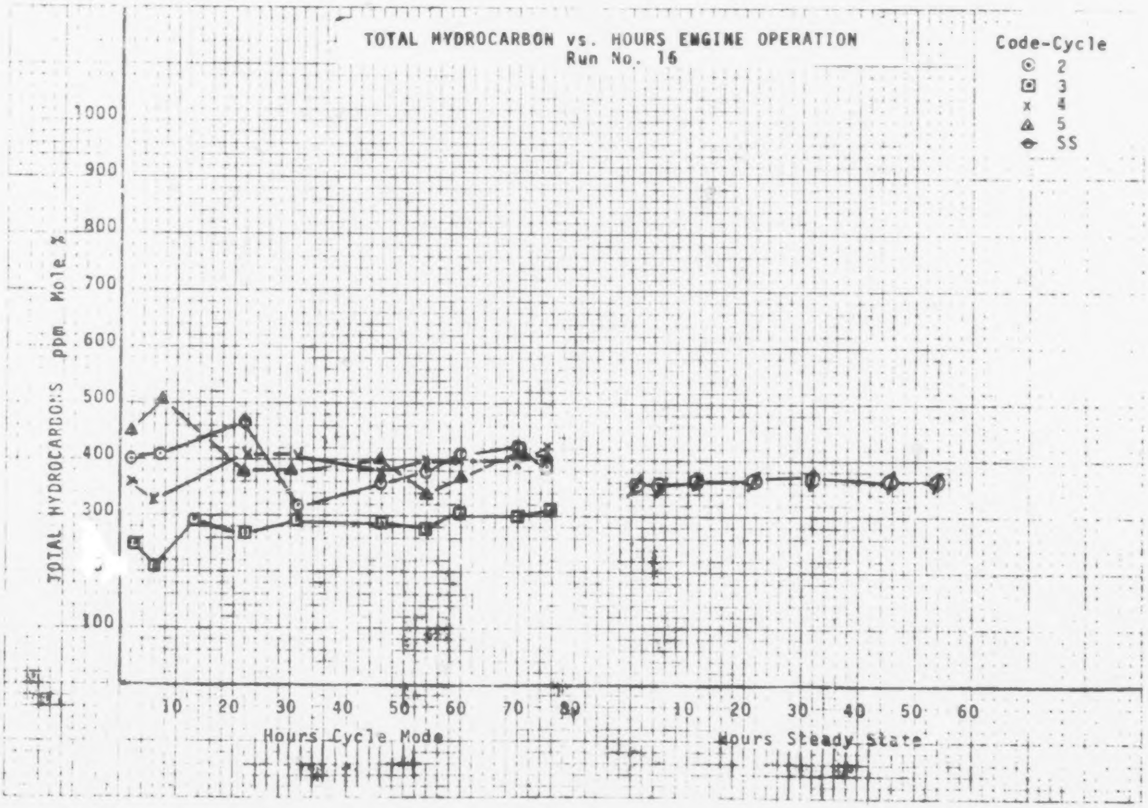

TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
RUN No. 9
Code-Cycle
⊙ 2
⊡ 3
x 4
▲ 5
◆ SS
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
Hours Cycle Mode
10
20
30
40
50
60
Hours Steady State

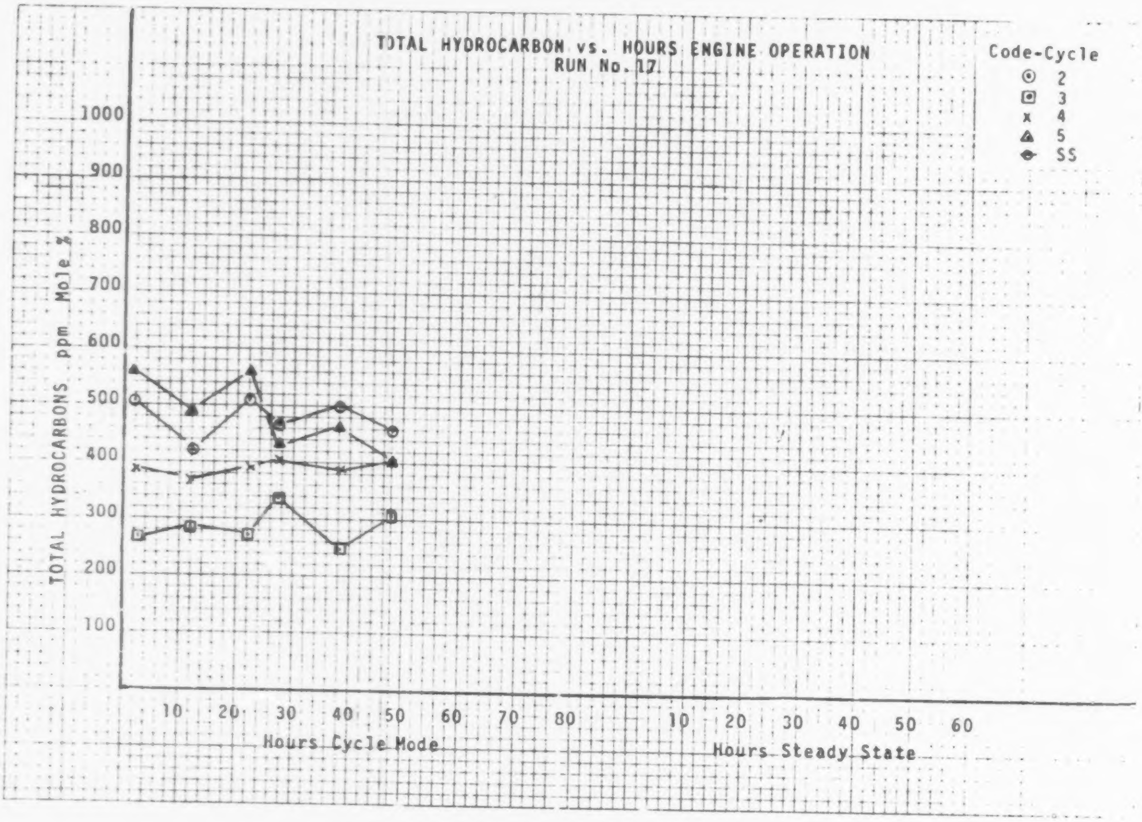

TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
RUN No. 11
Code-Cycle
⊙ 2
⊡ 3
x 4
▲ 5
◆ SS
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
Hours Cycle Mode
10
20
30
40
50
60
Hours Steady State

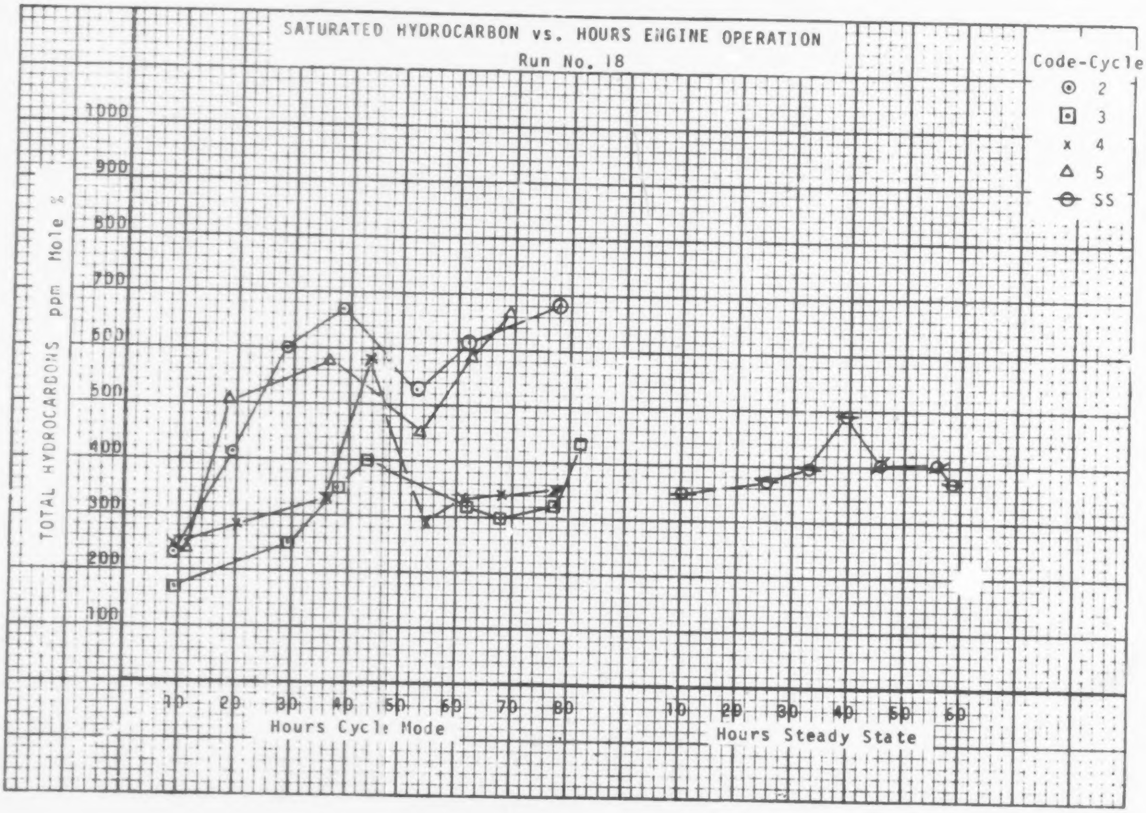

TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
RUN No. 12
Code-Cycle
⊙ 2
⊡ 3
x 4
▲ 5
⊖ SS
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
None
10 20 30 40 50 60 70 80
Hours Cycle Mode
10 20 30 40 50 60
Hours Steady State

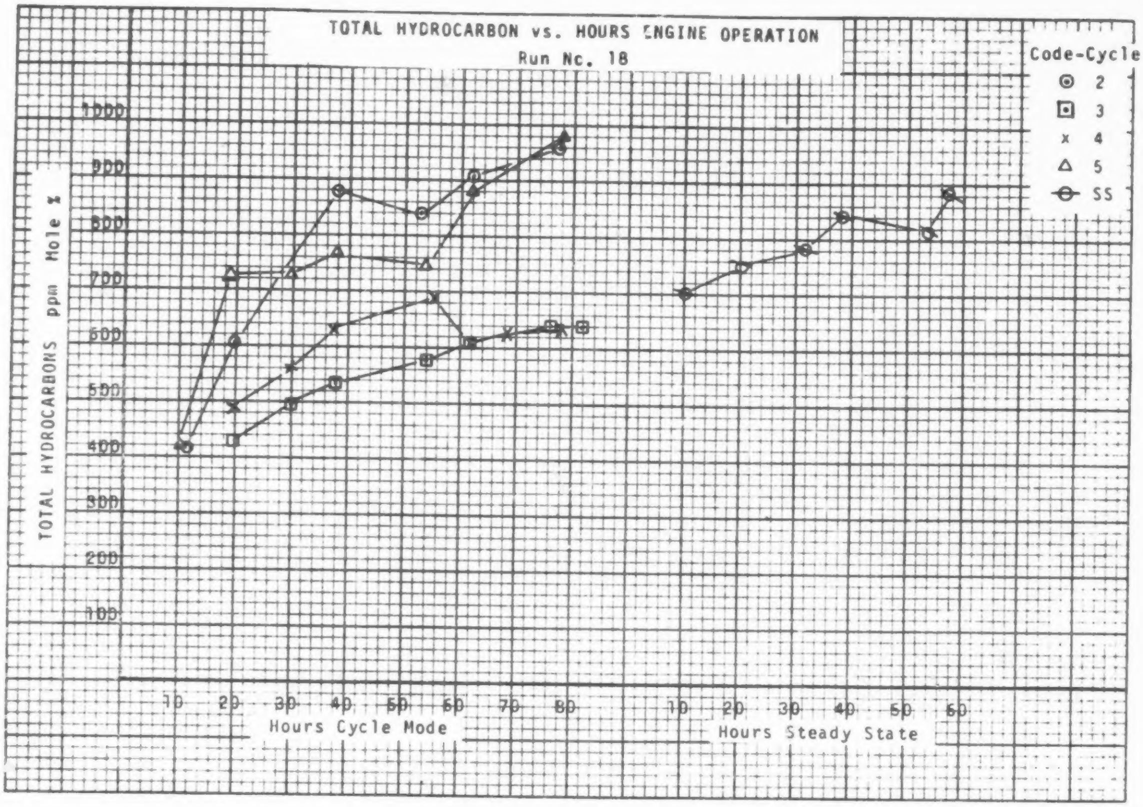

TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
RUN No. 13
Code-Cycle
⊙ 2
⊡ 3
x 4
△ 5
⊖ SS
1165
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
10 20 30 40 50 60 70 80
Hours Cycle Mode
10 20 30 40 50 60
Hours Steady State

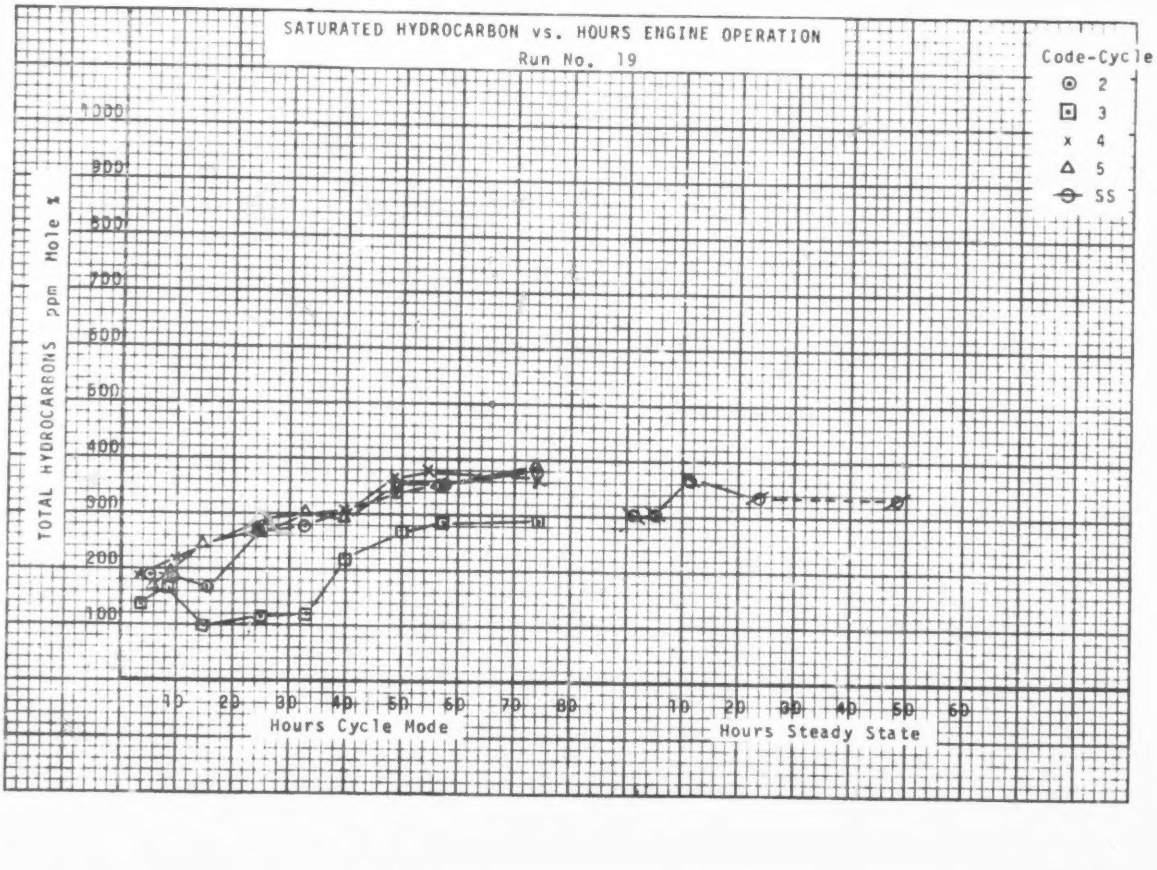

TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
RUN No. 14
Code-Cycle
◎ 2
▣ 3
x 4
▲ 5
◆ SS
TOTAL HYDROCARBONS ppm. Mole %
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
10
20
30
40
50
60
Hours Cycle Mode
Hours Steady State
None - 24 hours cycle
through tube only

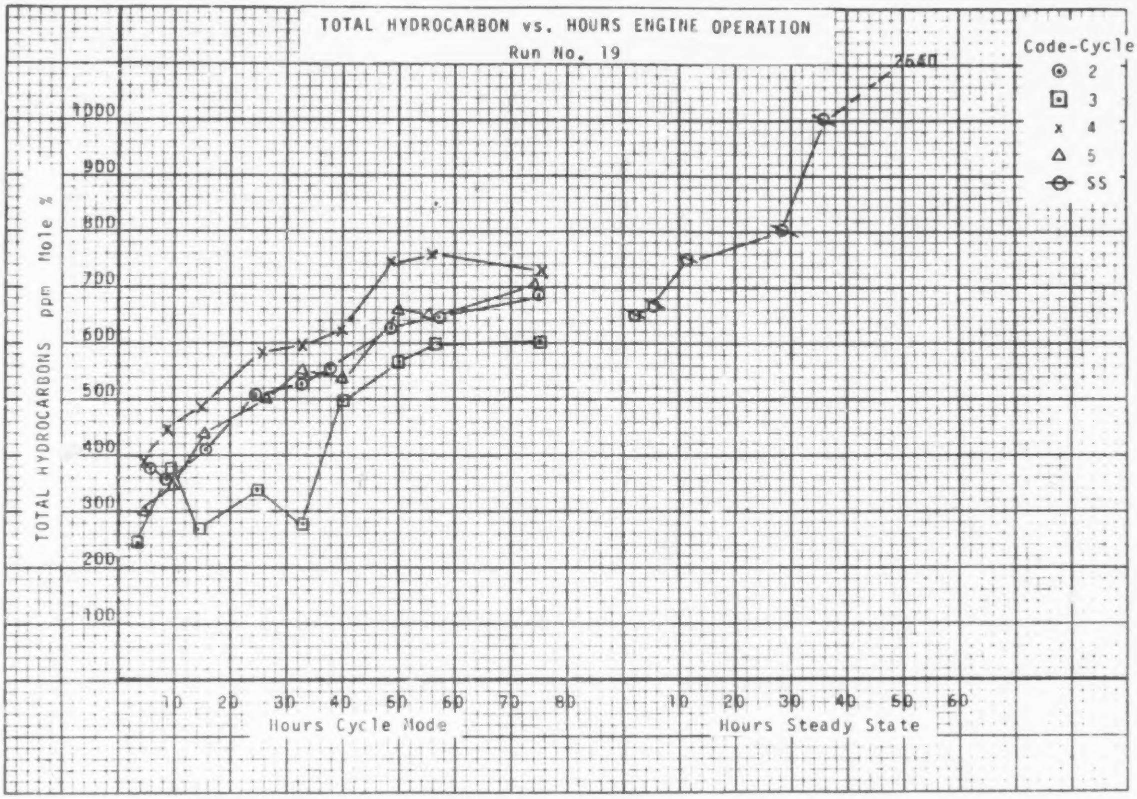

TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
Run No. 16
Code-Cycle
⊙ 2
▣ 3
x 4
△ 5
⊖ SS
TOTAL HYDROCARBONS ppm. Mole %
1000
900
800
700
600
500
400
300
100
10
20
30
40
50
60
70
80
10
20
30
40
50
60
Hours Cycle Mode
Hours Steady State

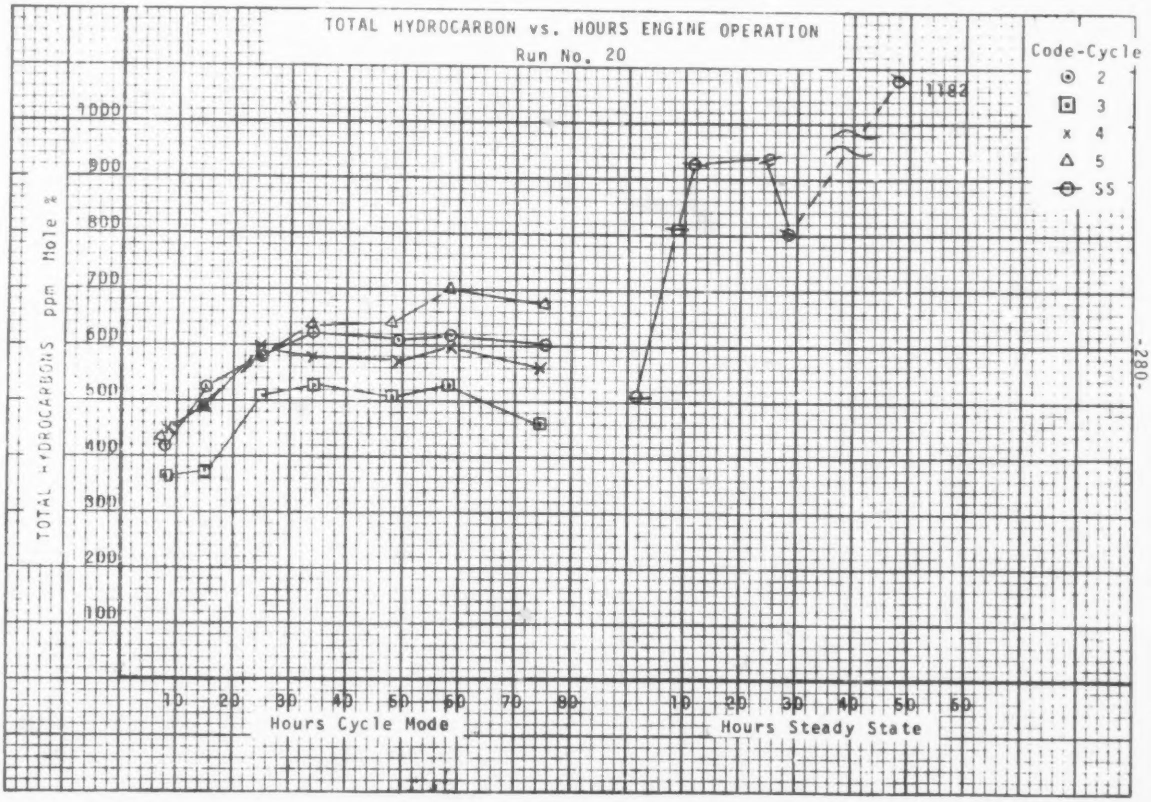

TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
RUN No. 17
Code-Cycle
⊙ 2
⊡ 3
x 4
▲ 5
⊖ SS
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
Hours Cycle Mode
10
20
30
40
50
60
Hours Steady State

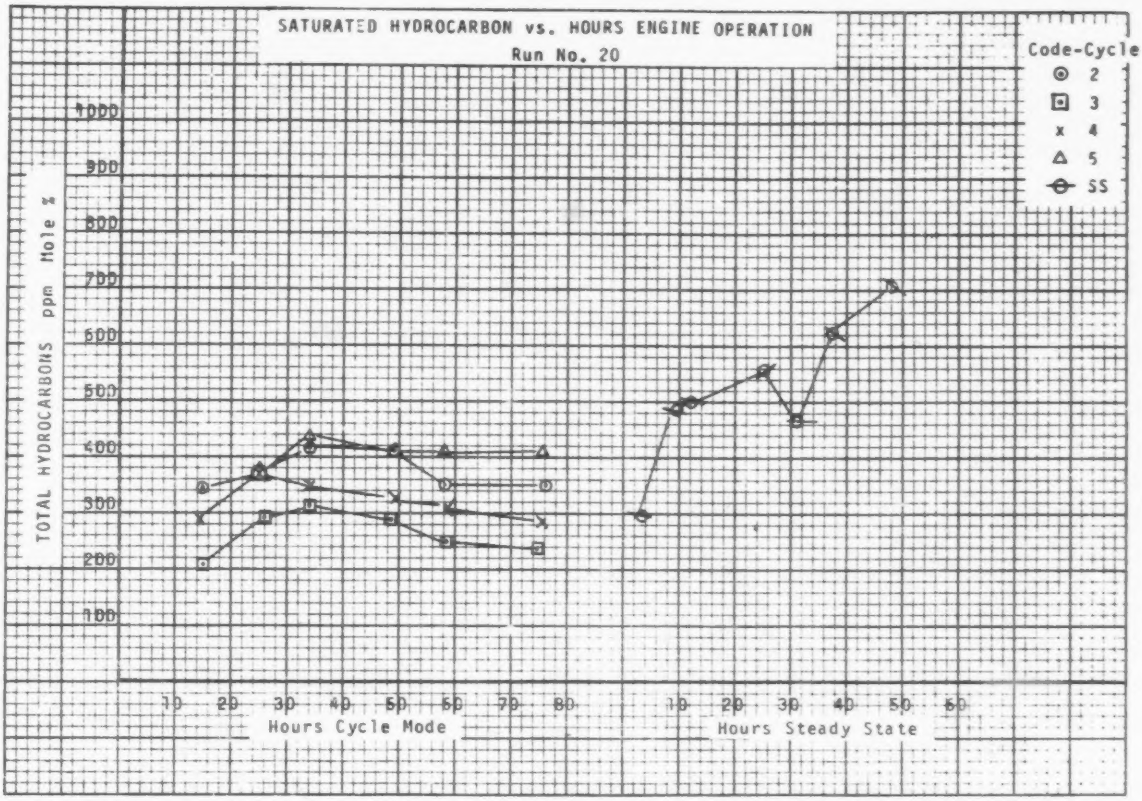

SATURATED HYDROCARBON vs. HOURS ENGINE OPERATION
Run No. 18
Code-Cycle
⊙ 2
⊡ 3
x 4
△ 5
⊖ SS
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
Hours Cycle Mode
10
20
30
40
50
60
Hours Steady State

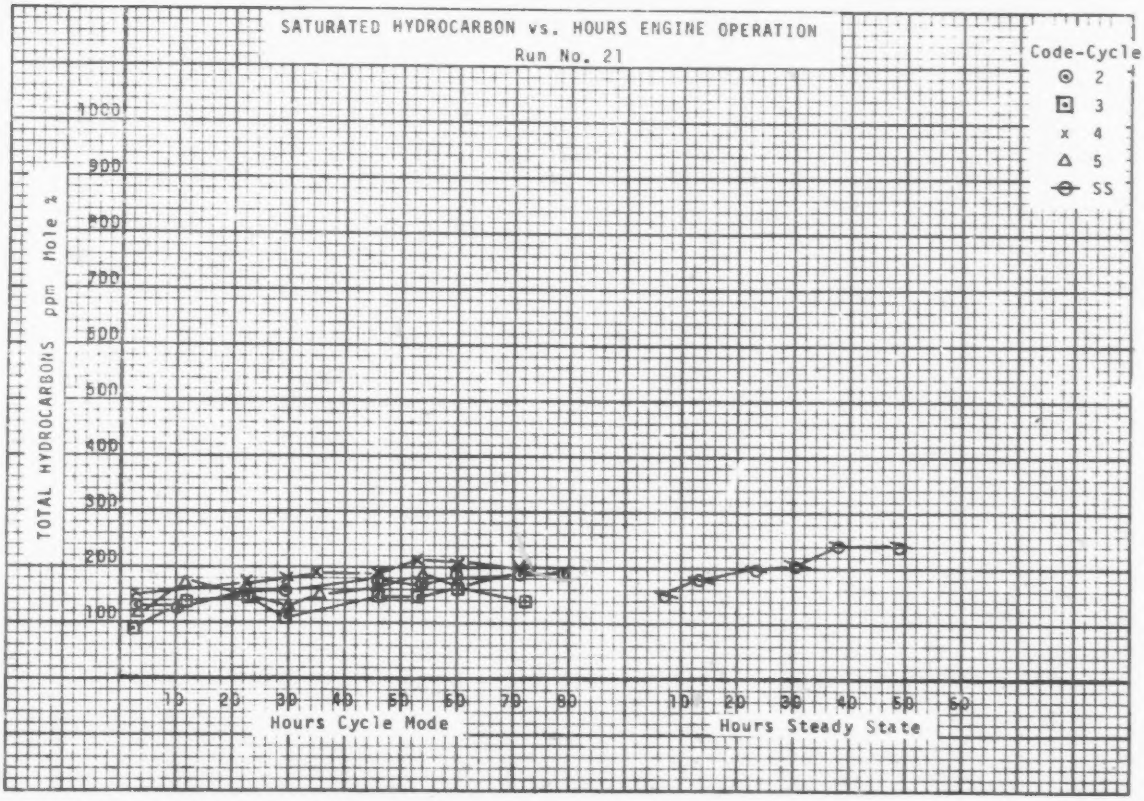

TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
Run No. 18
Code-Cycle
⊙ 2
⊡ 3
x 4
△ 5
-⊖- SS
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
Hours Cycle Mode
10
20
30
40
50
60
Hours Steady State

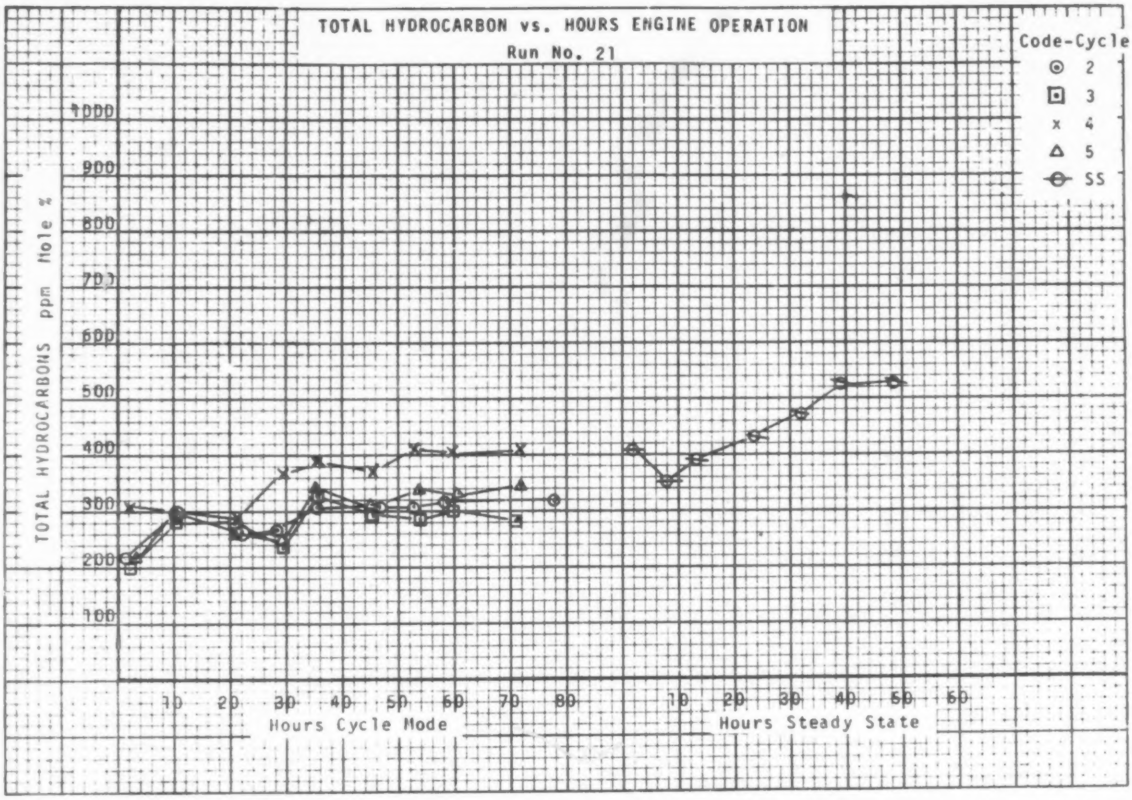

SATURATED HYDROCARBON vs. HOURS ENGINE OPERATION
Run No. 19
Code-Cycle
⊙ 2
⊡ 3
x 4
△ 5
-⊖- SS
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
Hours Cycle Mode
10
20
30
40
50
60
Hours Steady State

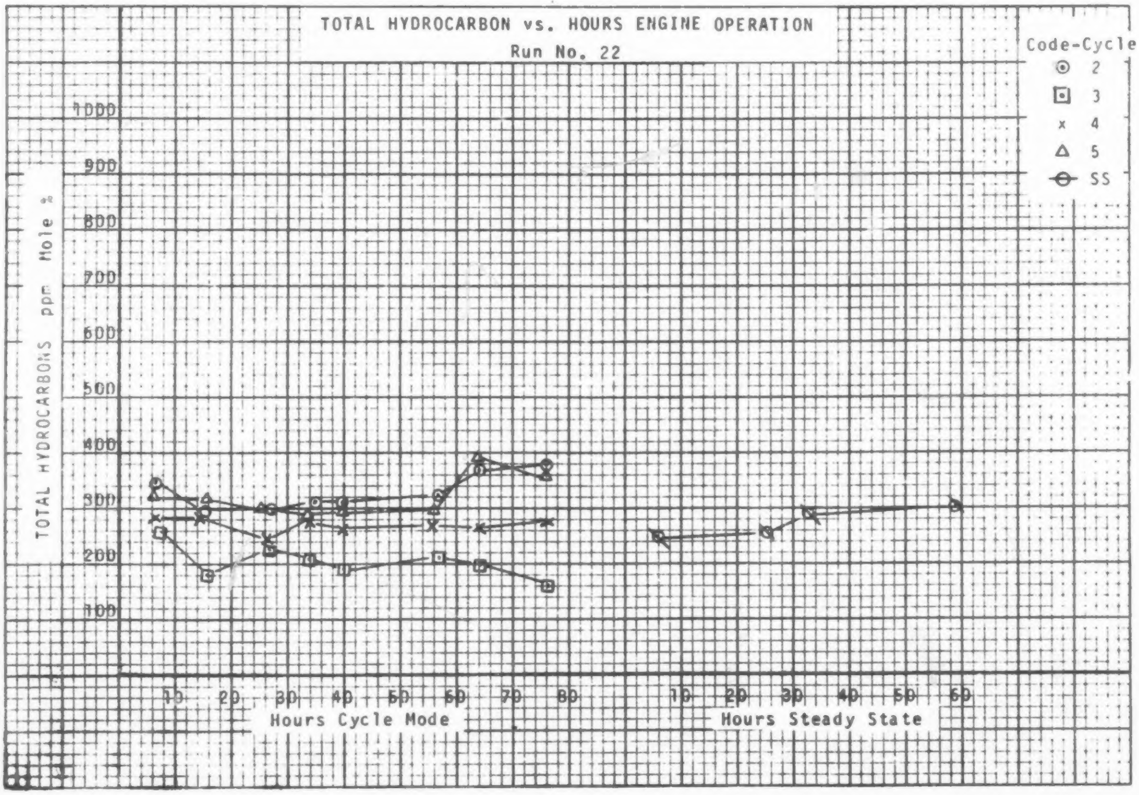

TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
Run No. 19
Code-Cycle
⊙ 2
⊡ 3
x 4
Δ 5
-θ- SS
2540
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
Hours Cycle Mode
10
20
30
40
50
60
Hours Steady State

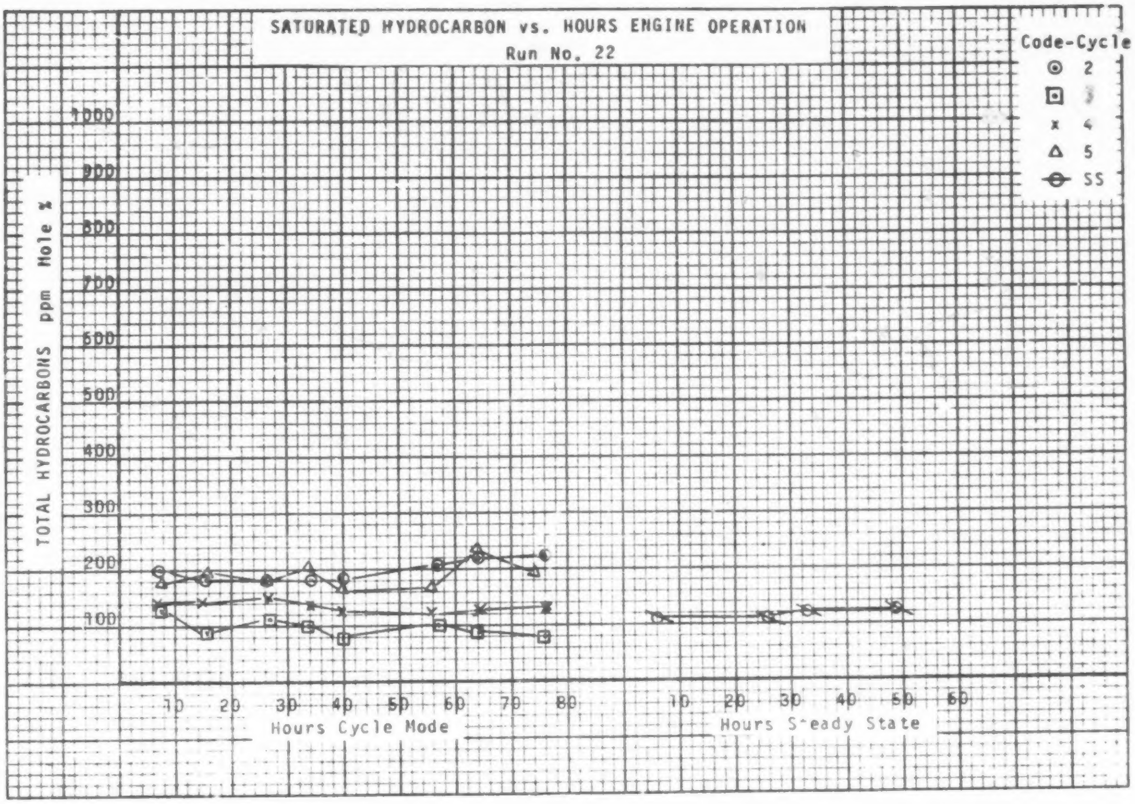

TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
Run No. 20
Code-Cycle
⊙ 2
⊡ 3
x 4
Δ 5
-θ- SS
1182
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
Hours Cycle Mode
10
20
30
40
50
60
Hours Steady State

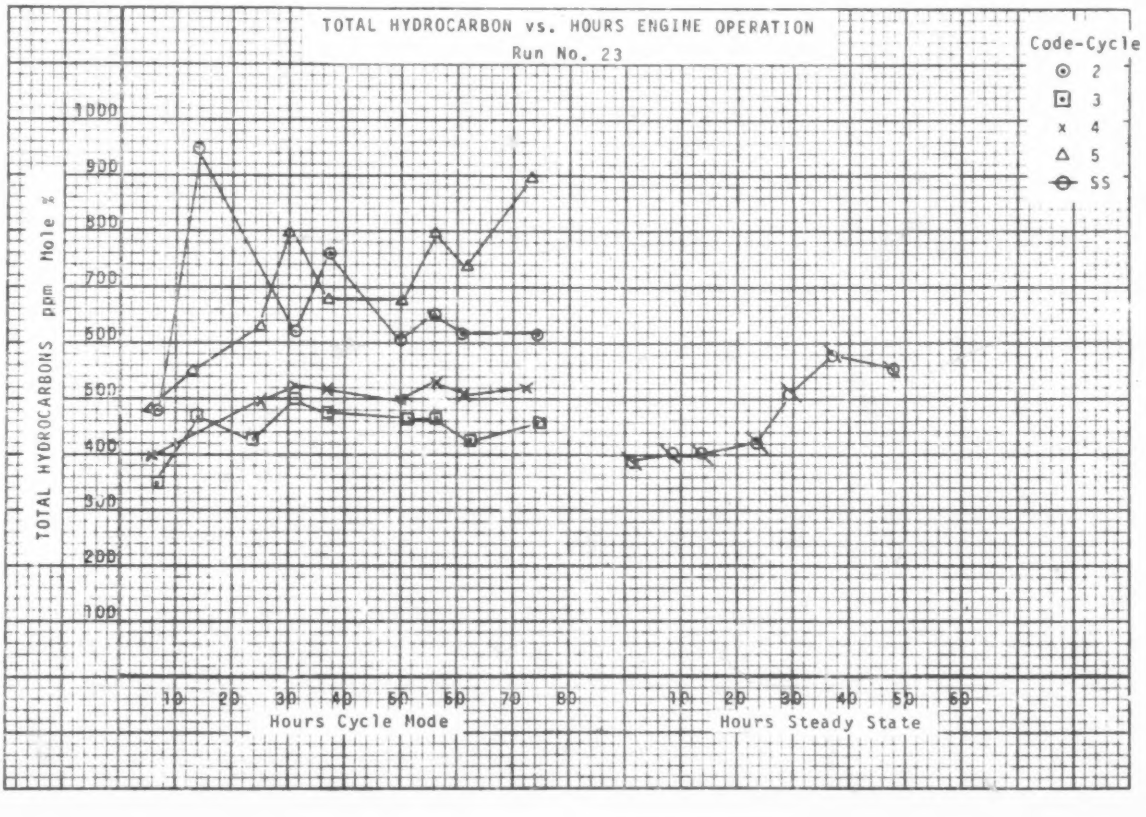

SATURATED HYDROCARBON vs. HOURS ENGINE OPERATION
Run No. 20
Code-Cycle
⊙ 2
⊡ 3
x 4
△ 5
SS
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
Hours Cycle Mode
10
20
30
40
50
60
Hours Steady State

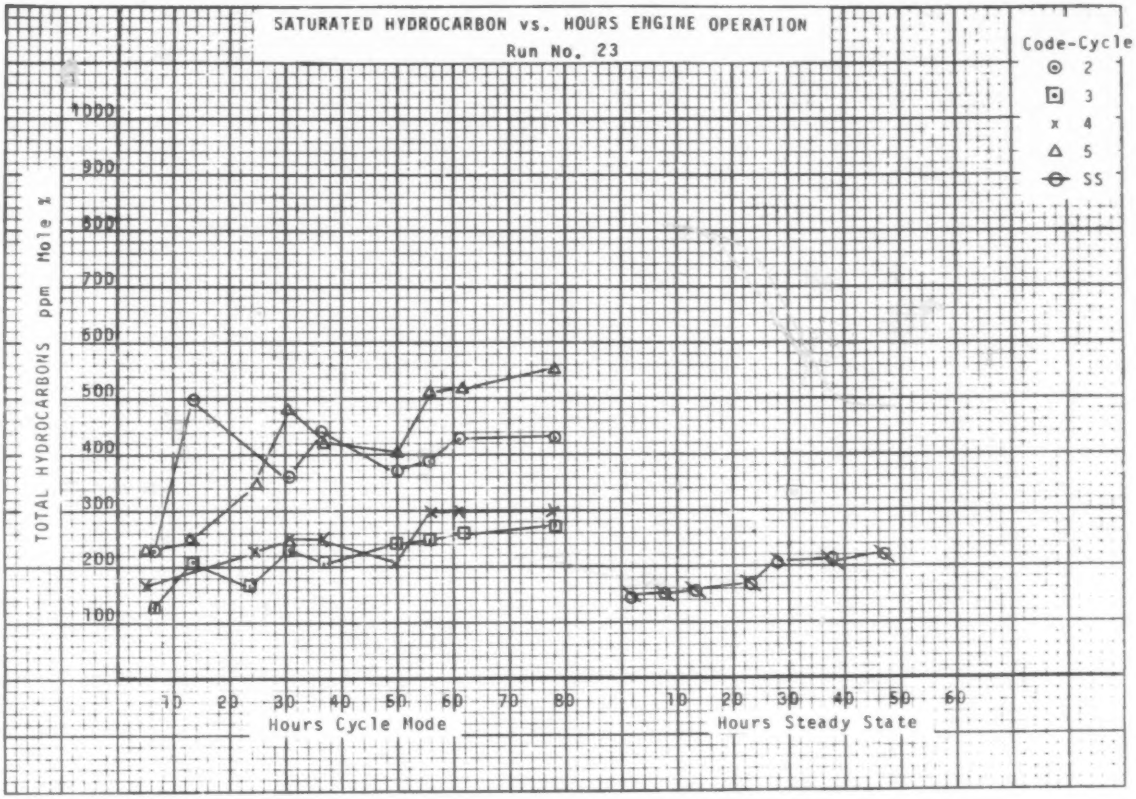

SATURATED HYDROCARBON vs. HOURS ENGINE OPERATION
Run No. 21
Code-Cycle
⊙ 2
⊡ 3
x 4
△ 5
SS
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
Hours Cycle Mode
10
20
30
40
50
60
Hours Steady State

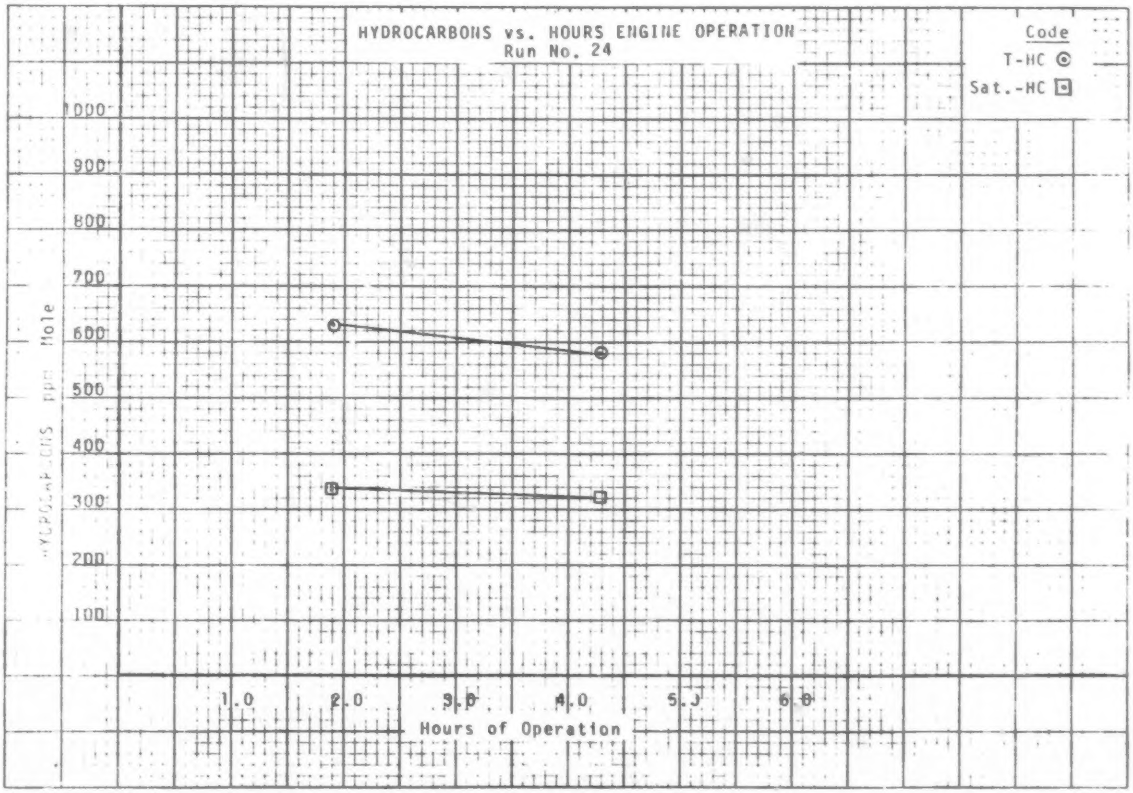

TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
Run No. 21
Code-Cycle
⊙ 2
⊡ 3
x 4
△ 5
-⊖- SS
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
Hours Cycle Mode
10
20
30
40
50
60
Hours Steady State

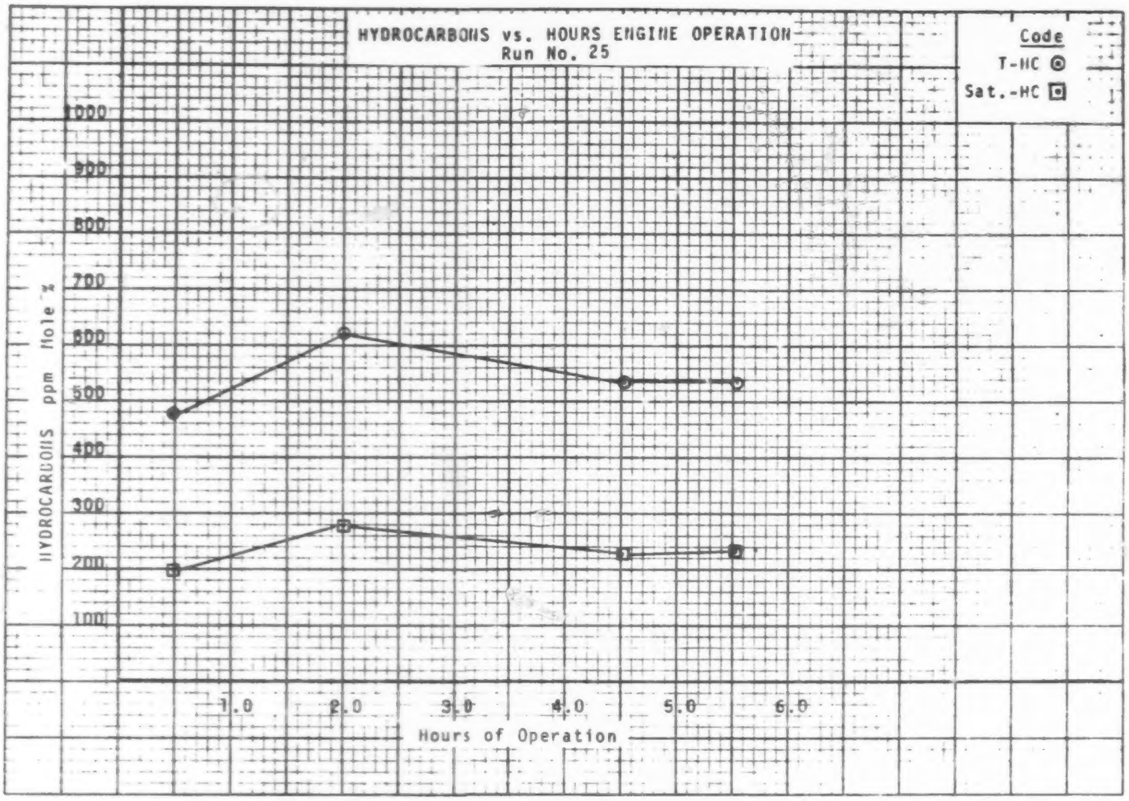

TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
Run No. 22
Code-Cycle
⊙ 2
⊡ 3
x 4
△ 5
-⊖- SS
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
Hours Cycle Mode
10
20
30
40
50
60
Hours Steady State

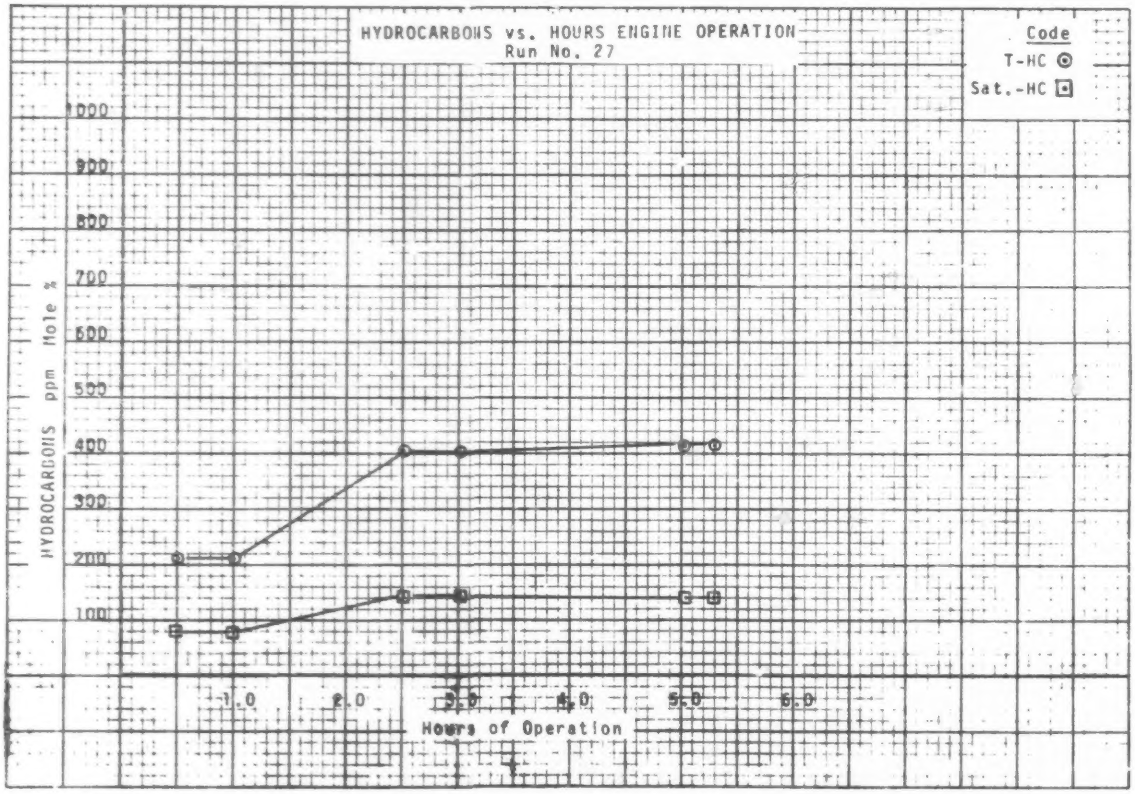

SATURATED HYDROCARBON vs. HOURS ENGINE OPERATION
Run No. 22
Code-Cycle
⊙ 2
⊡ 3
x 4
△ 5
⊖ SS
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
Hours Cycle Mode
10
20
30
40
50
60
Hours Steady State

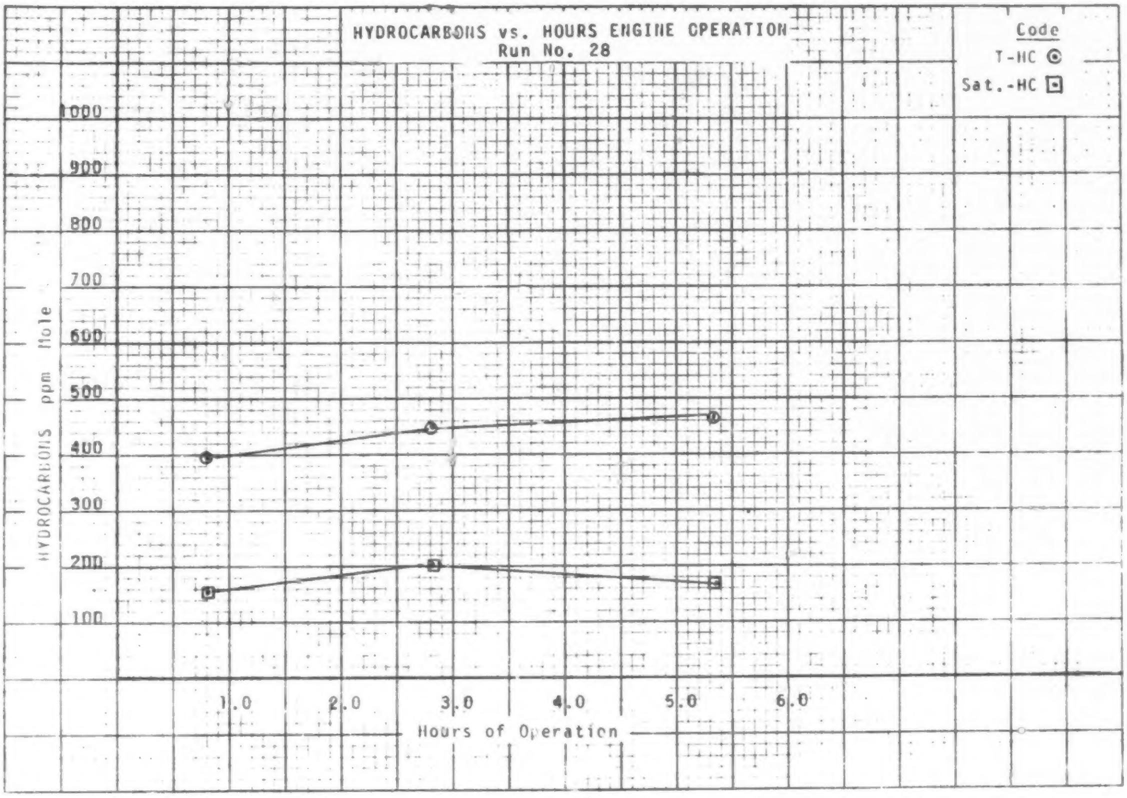

TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
Run No. 23
Code-Cycle
⊙ 2
⊡ 3
x 4
△ 5
⊖ SS
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
Hours Cycle Mode
10
20
30
40
50
60
Hours Steady State


SATURATED HYDROCARBON vs. HOURS ENGINE OPERATION
Run No. 23
Code-Cycle
⊙ 2
⊡ 3
x 4
△ 5
-⊖- SS
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
Hours Cycle Mode
10
20
30
40
50
60
Hours Steady State

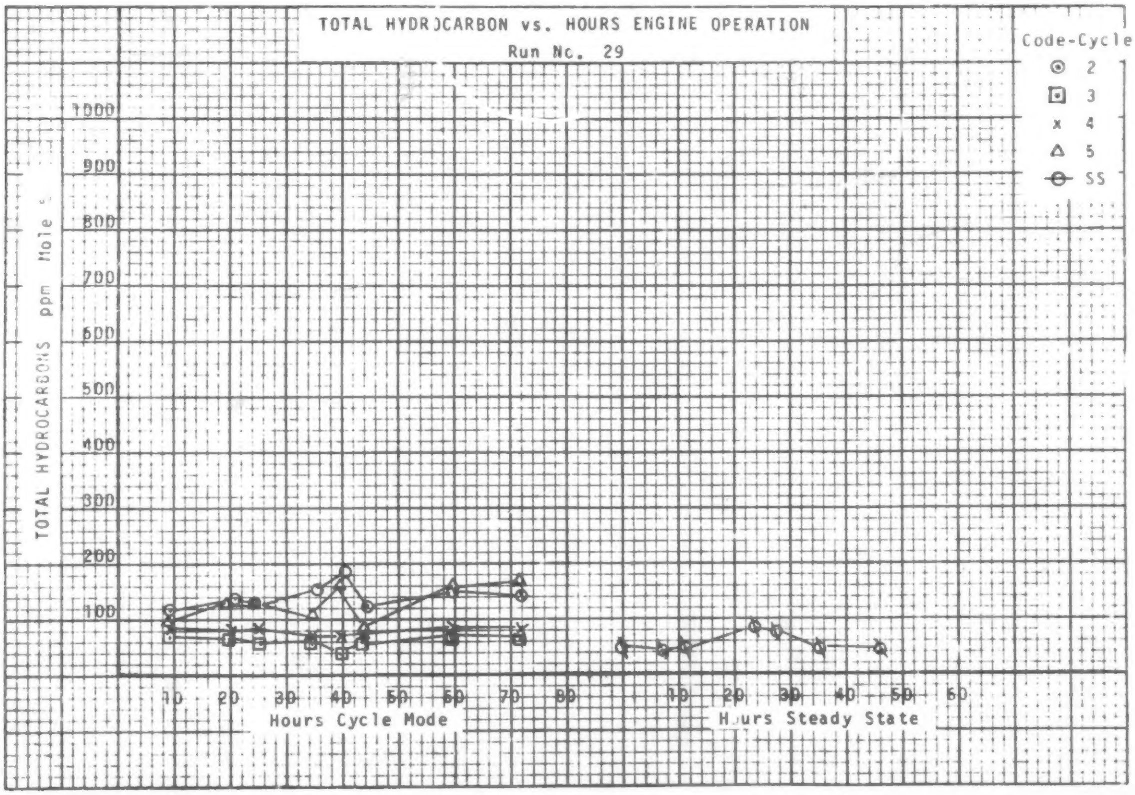

HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 24
Code
T-HC ⊙
Sat.-HC ⊡
HYDROCARBONS ppm Mole
1000
900
800
700
600
500
400
300
200
100
1.0
2.0
3.0
4.0
5.0
6.0
Hours of Operation


HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 25
Code
T-HC ⊙
Sat.-HC ⊡
HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
1.0
2.0
3.0
4.0
5.0
6.0
Hours of Operation

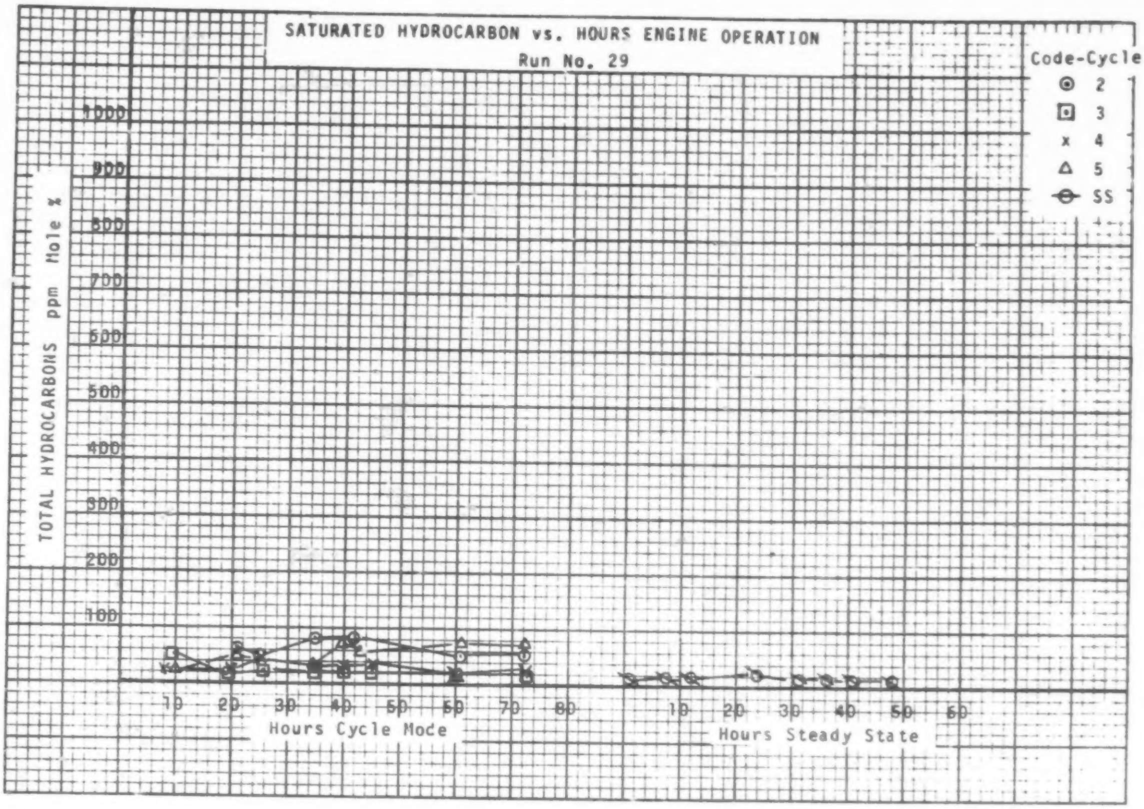

HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 27
Code
T-HC ⊙
Sat.-HC ⊡
HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
1.0
2.0
3.0
4.0
5.0
6.0
Hours of Operation

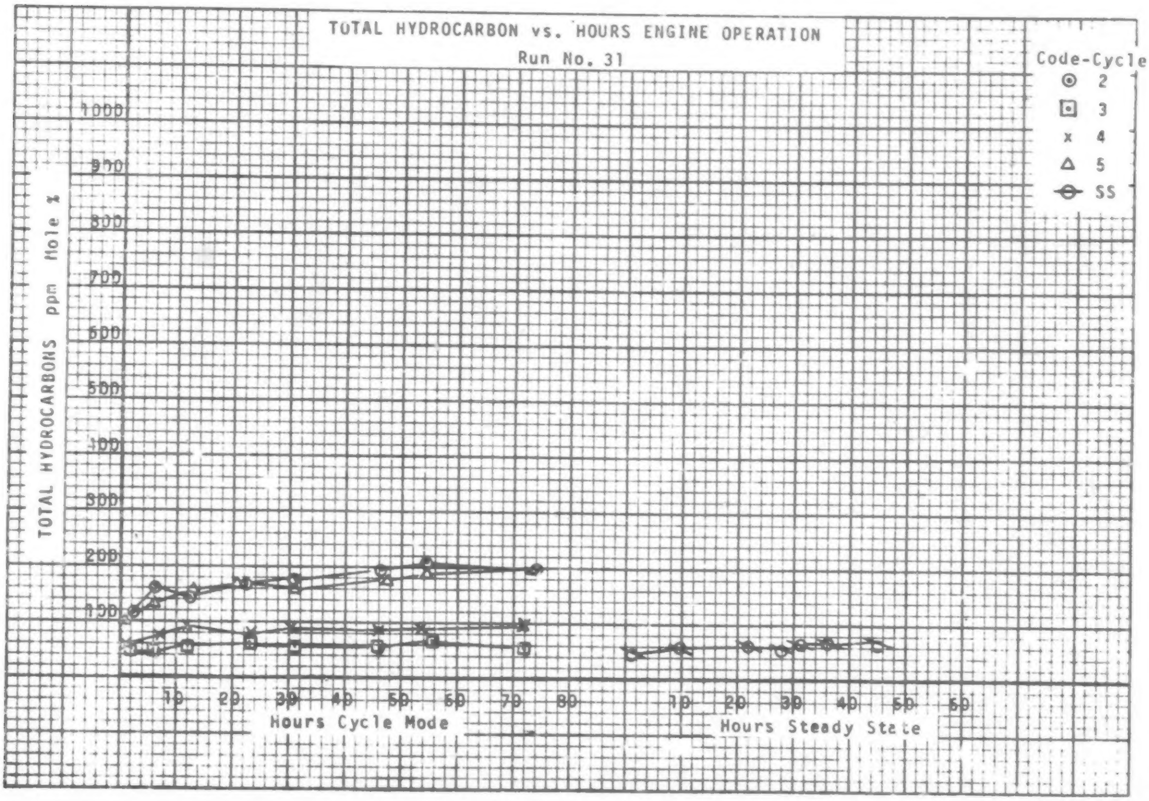


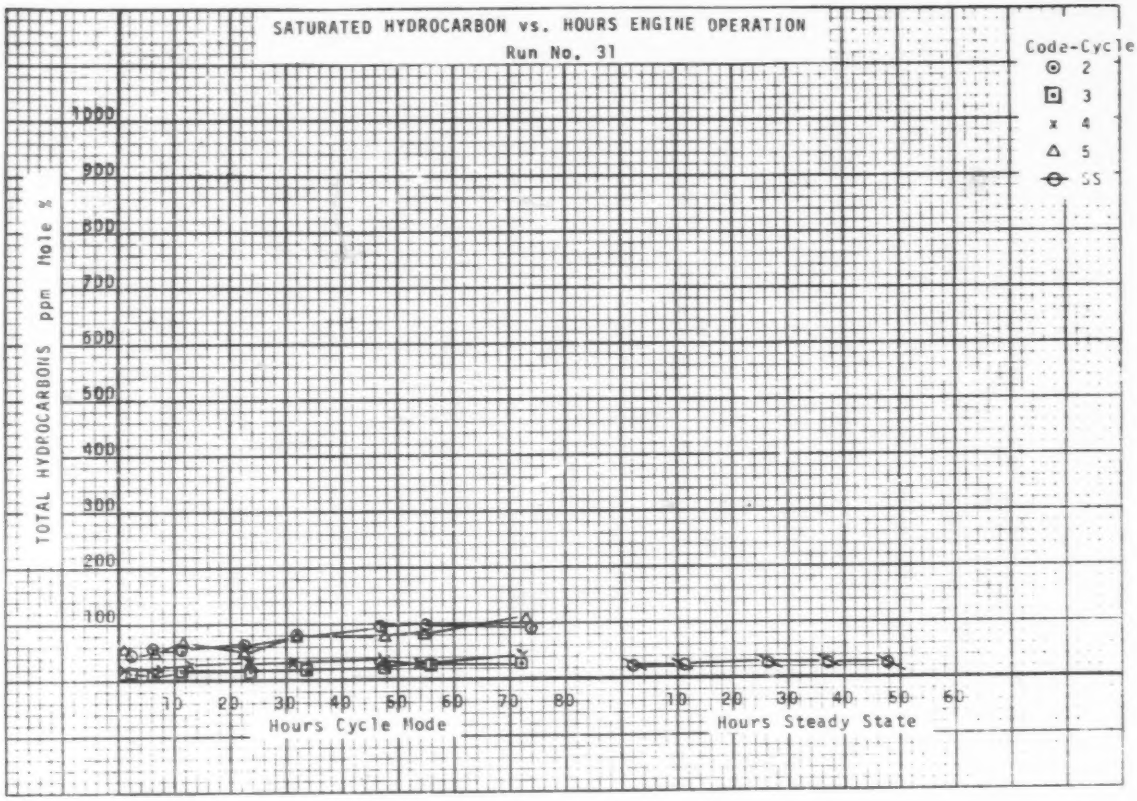
HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 28



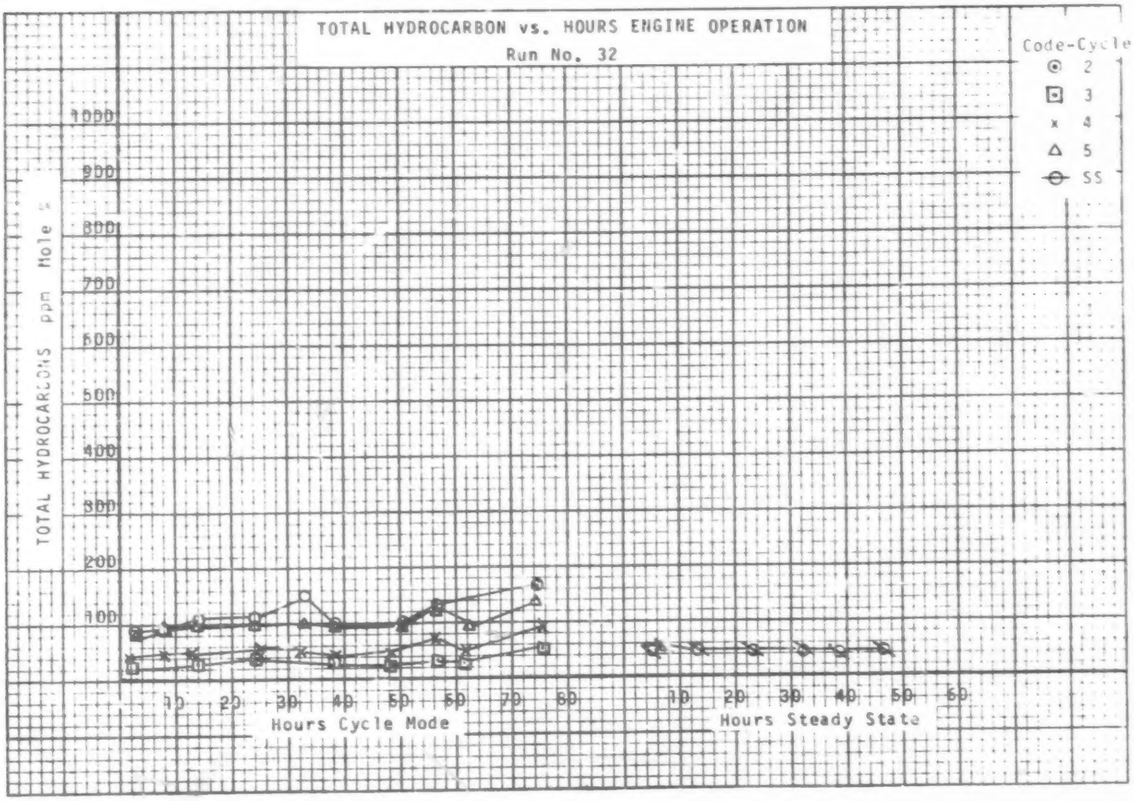
TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
Run No. 29


SATURATED HYDROCARBON vs. HOURS ENGINE OPERATION
Run No. 29
Code-Cycle
⊙ 2
⊡ 3
x 4
△ 5
SS
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
Hours Cycle Mode
10
20
30
40
50
60
Hours Steady State

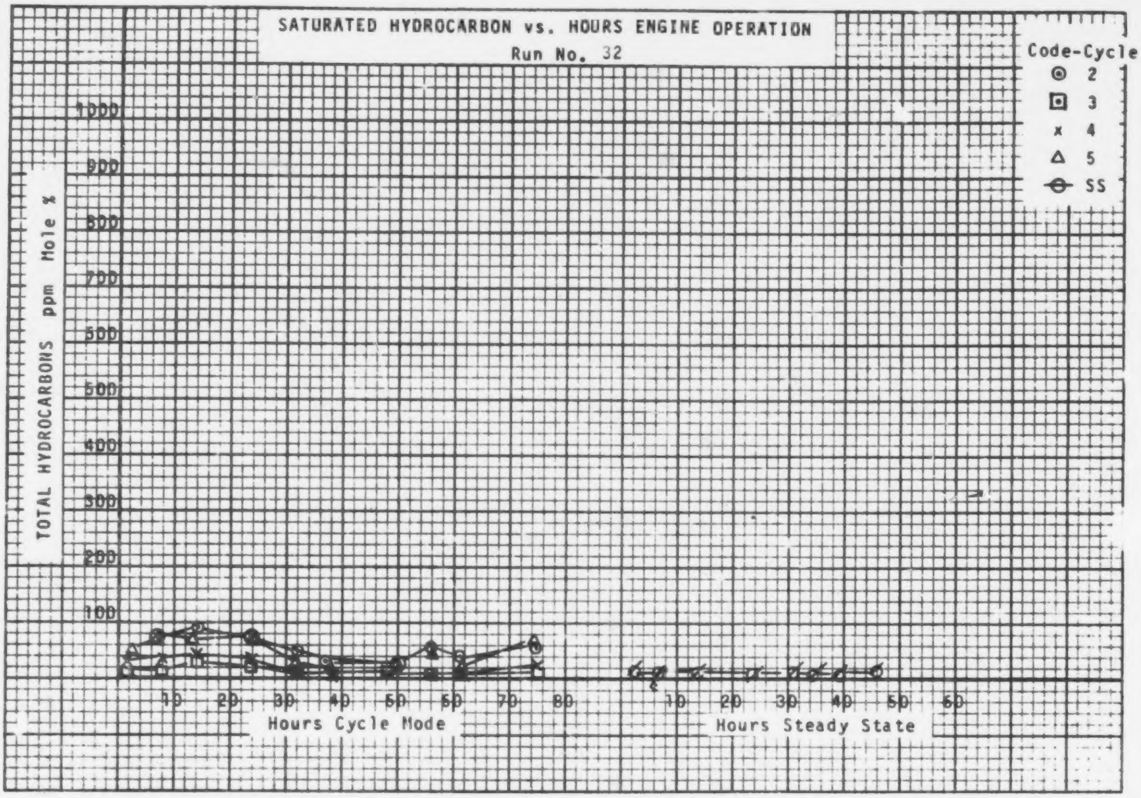

TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
Run No. 31
Code-Cycle
⊙ 2
⊡ 3
x 4
△ 5
SS
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
Hours Cycle Mode
10
20
30
40
50
60
Hours Steady State

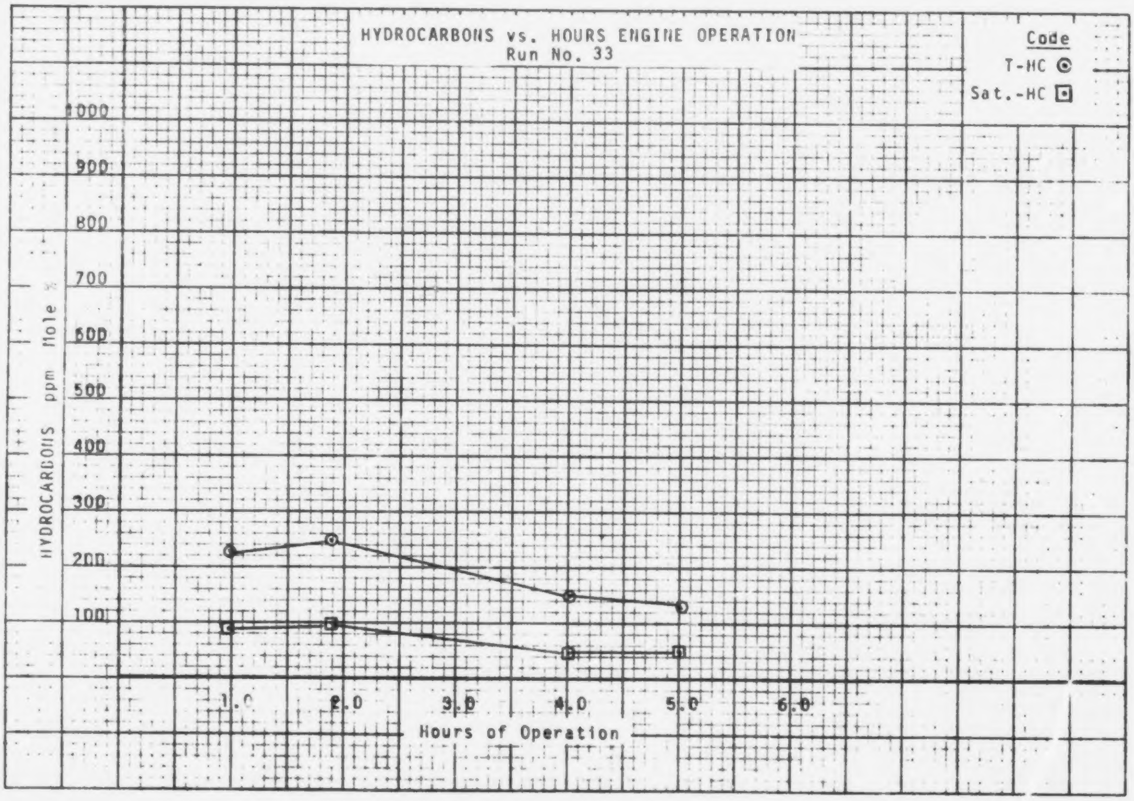


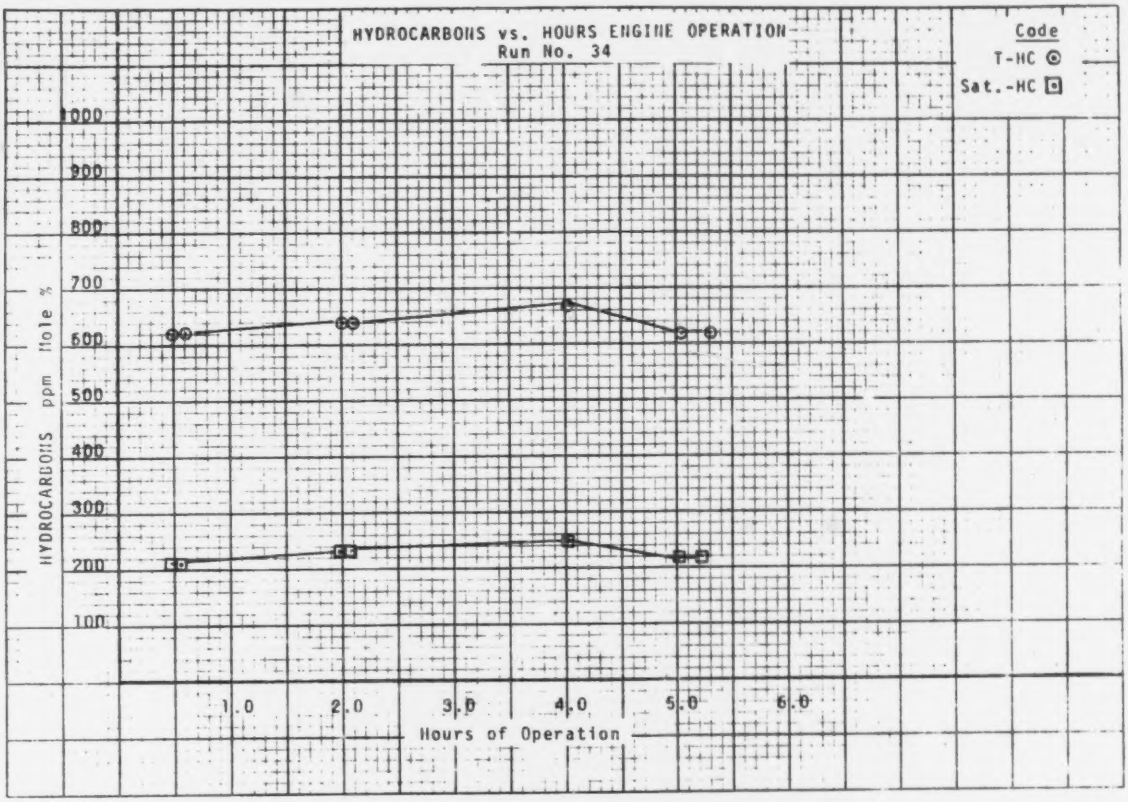
SATURATED HYDROCARBON vs. HOURS ENGINE OPERATION
Run No. 31

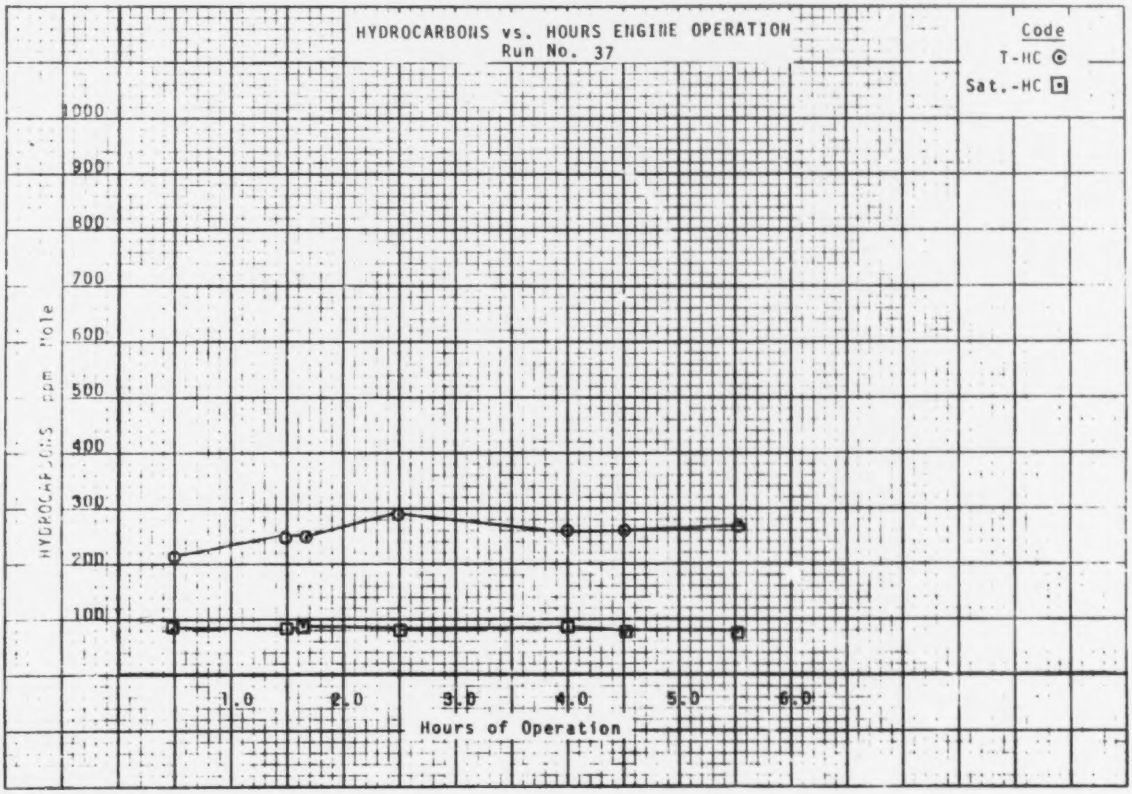


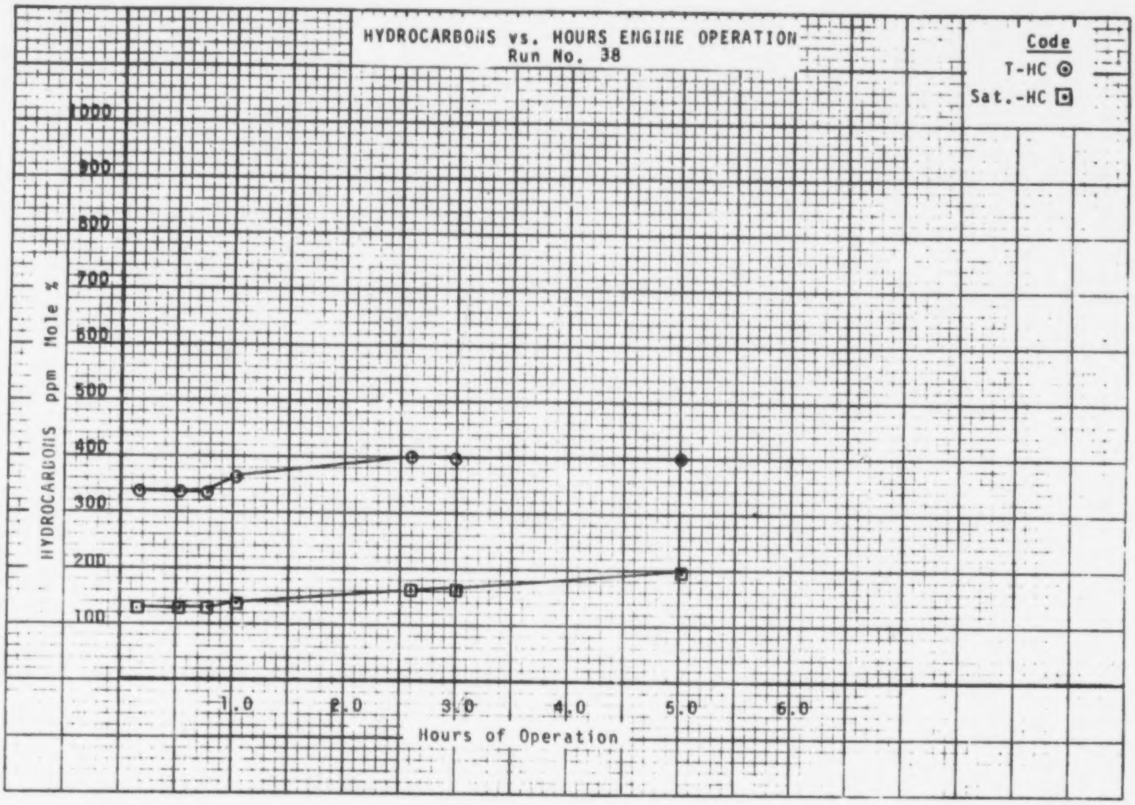
TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
Run No. 32

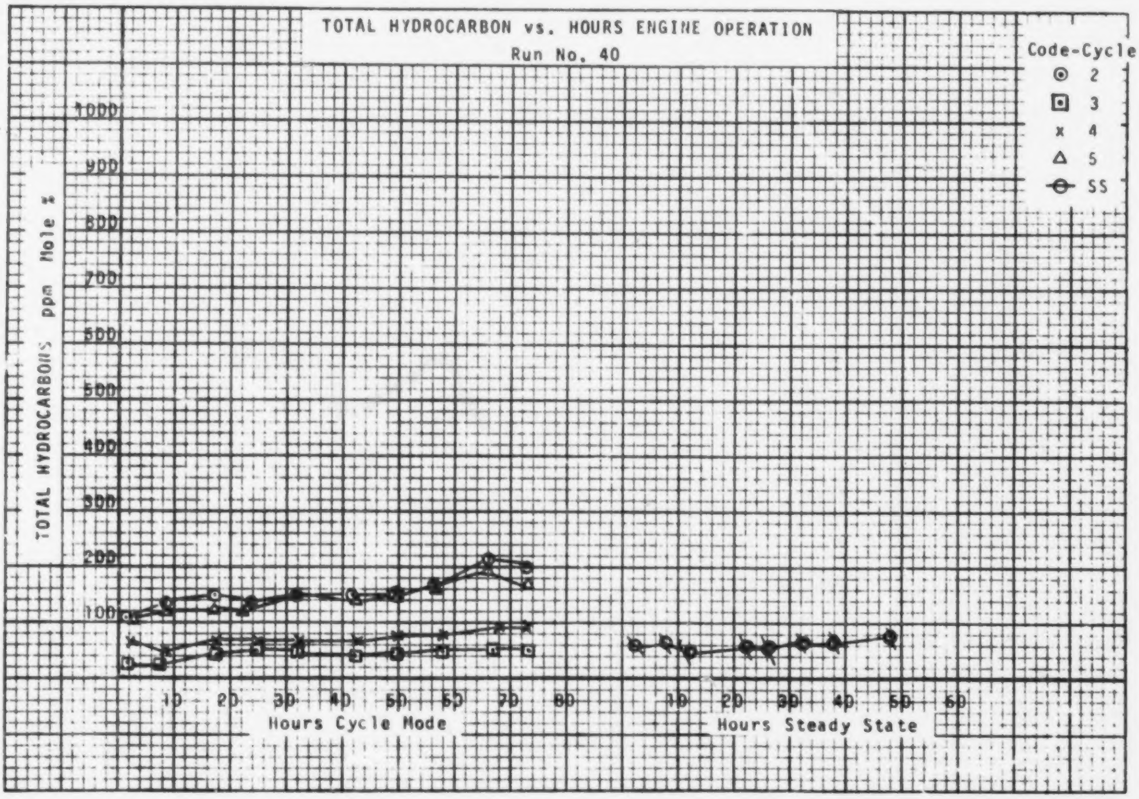

SATURATED HYDROCARBON vs. HOURS ENGINE OPERATION
Run No. 32
Code-Cycle
⊙ 2
⊡ 3
x 4
△ 5
-⊖- SS
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
Hours Cycle Mode
10
20
30
40
50
60
Hours Steady State

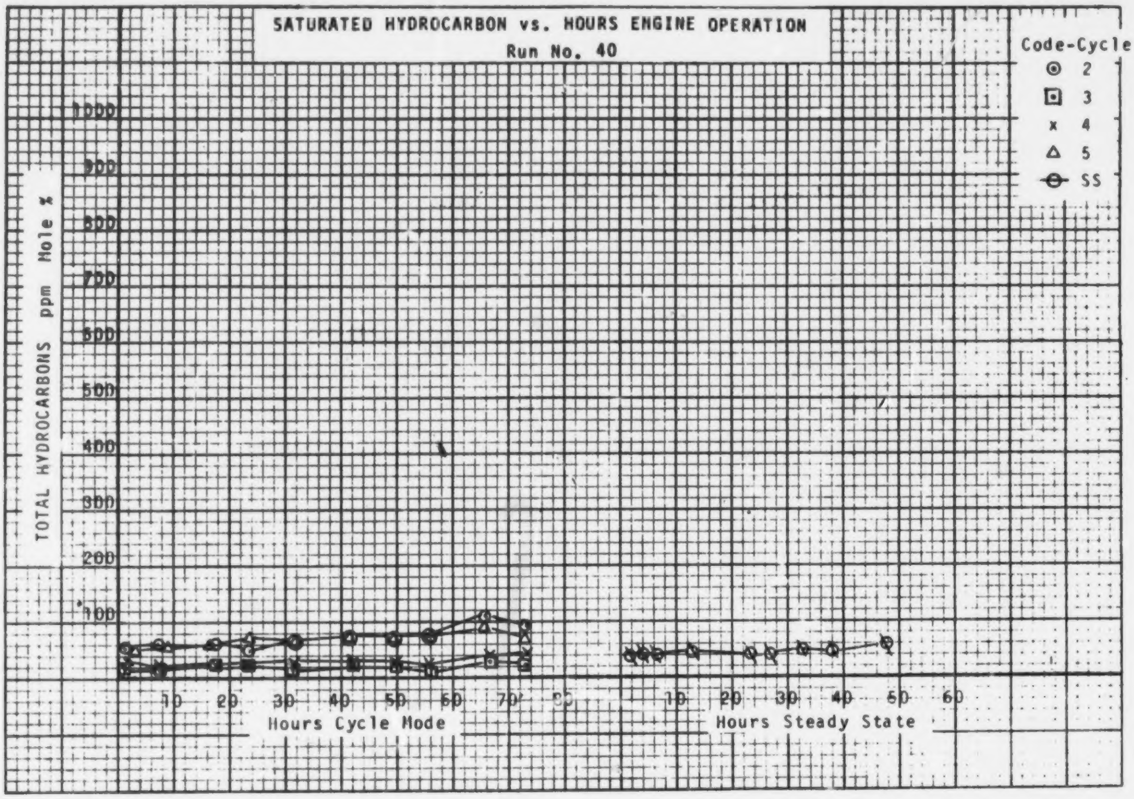

HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 33
Code
T-HC ⊙
Sat.-HC ⊡
HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
1.0
2.0
3.0
4.0
5.0
6.0
Hours of Operation

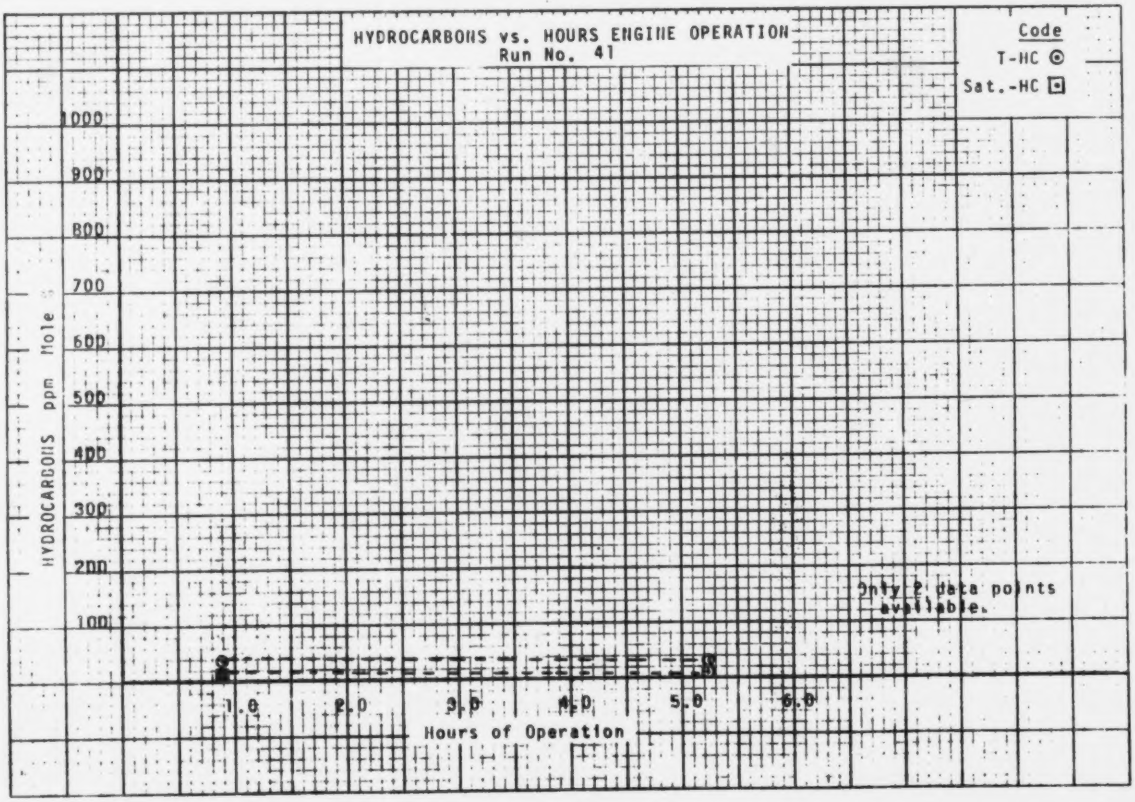

HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 34
Code
T-HC ⊙
Sat.-HC ⊡
HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
1.0
2.0
3.0
4.0
5.0
6.0
Hours of Operation

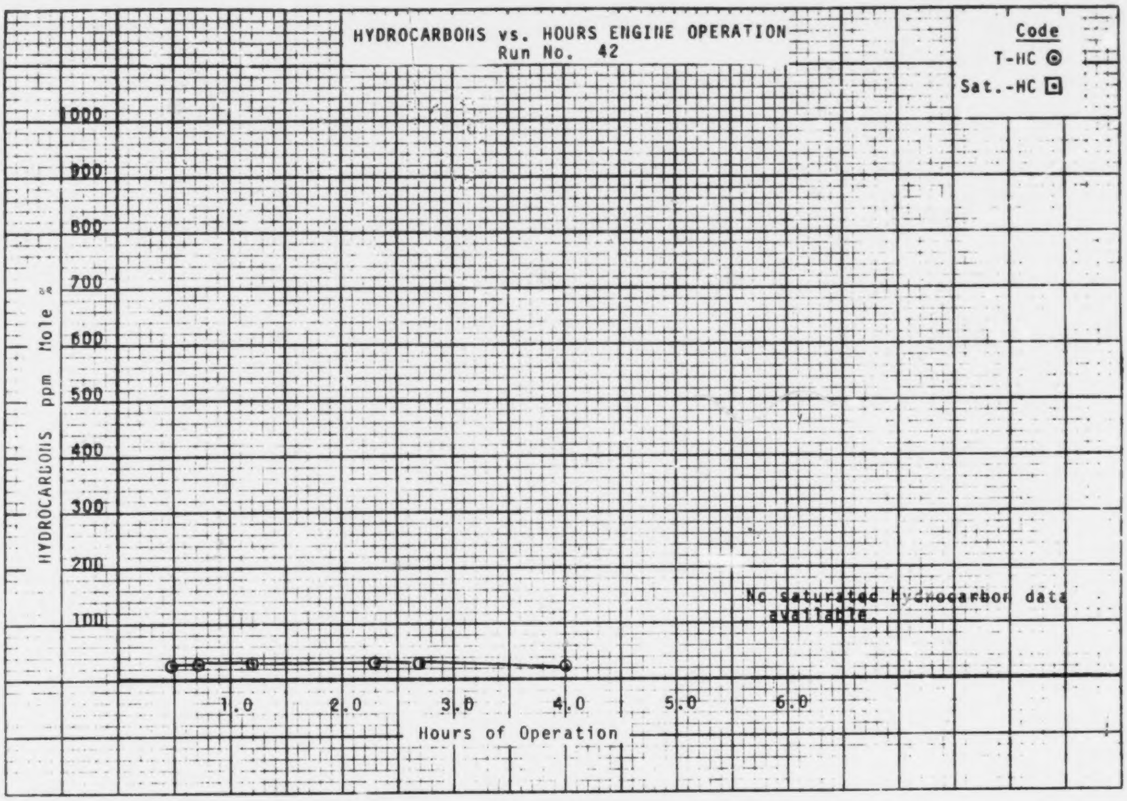

HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 37
Code
T-HC ⊙
Sat.-HC ⊡
HYDROCARBONS ppm Mole
1000
900
800
700
600
500
400
300
200
100
1.0
2.0
3.0
4.0
5.0
6.0
Hours of Operation

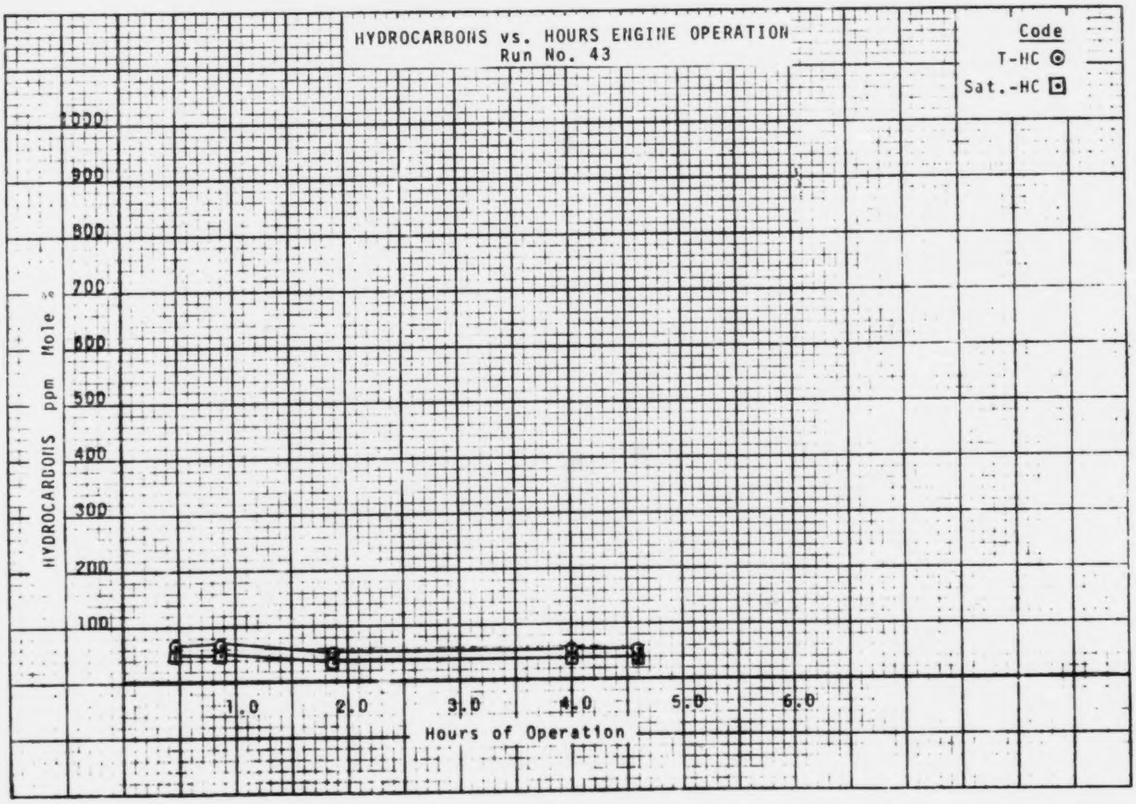

HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 38
Code
T-HC ⊙
Sat.-HC ⊡
HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
1.0
2.0
3.0
4.0
5.0
6.0
Hours of Operation

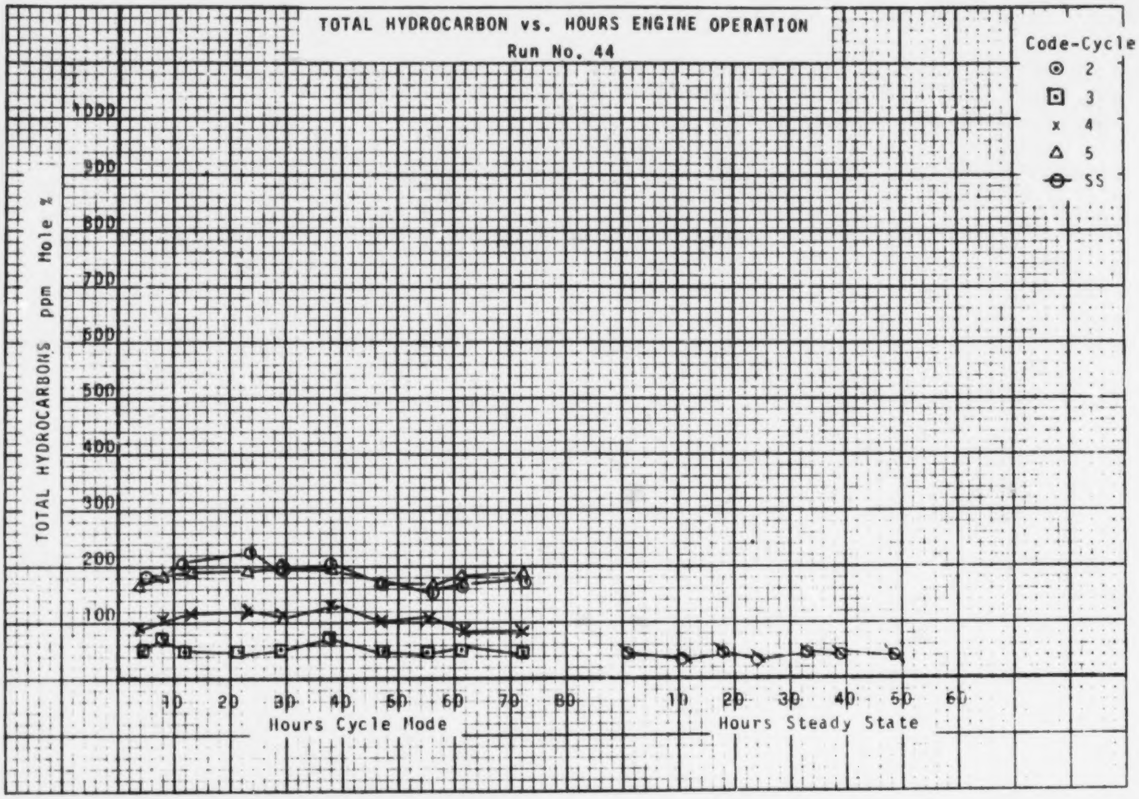

TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
Run No. 40
Code-Cycle
⊙ 2
⊡ 3
x 4
△ 5
SS
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
Hours Cycle Mode
10
20
30
40
50
60
Hours Steady State

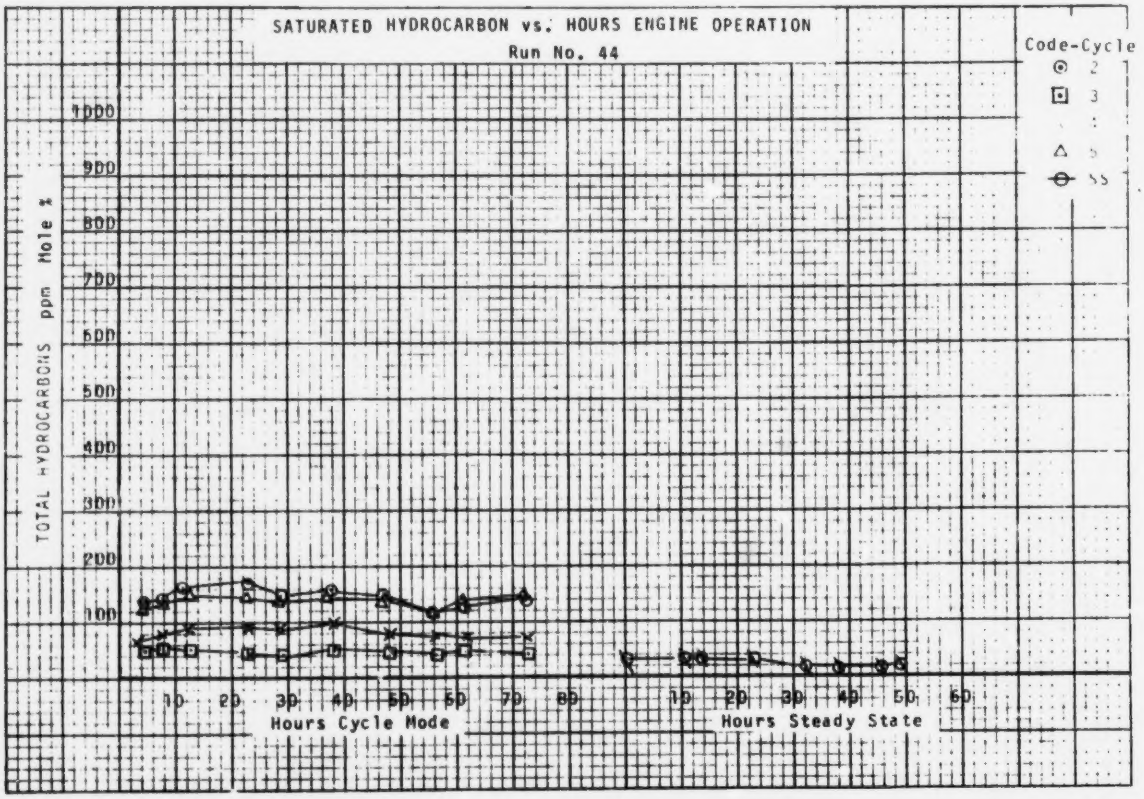

SATURATED HYDROCARBON vs. HOURS ENGINE OPERATION
Run No. 40
Code-Cycle
⊙ 2
⊡ 3
x 4
△ 5
-⊖- SS
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
Hours Cycle Mode
10
20
30
40
50
60
Hours Steady State

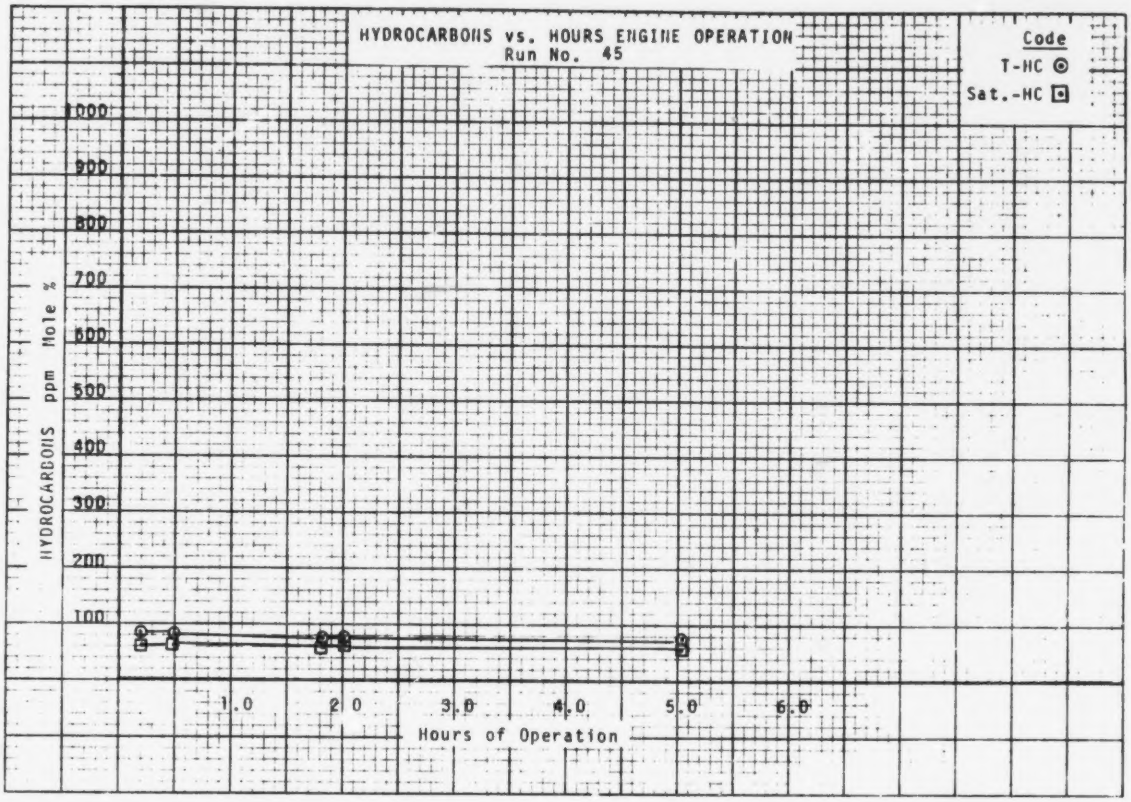

HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 41
Code
T-HC ⊙
Sat.-HC ⊡
HYDROCARBONS ppm Mole
1000
900
800
700
600
500
400
300
200
100
1.0
2.0
3.0
4.0
5.0
6.0
Hours of Operation
Only 2 data points available.

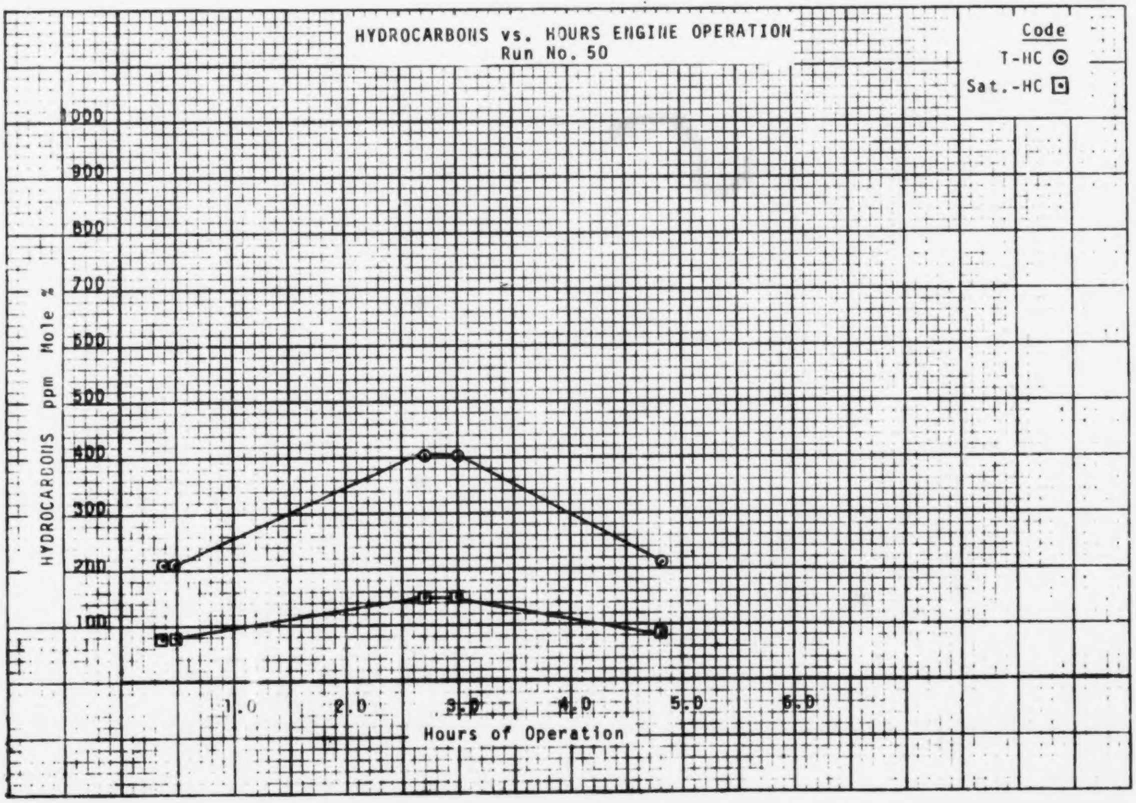

HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 42
Code
T-HC ⊙
Sat.-HC ⊡
HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
No saturated Hydrocarbon data available.
1.0
2.0
3.0
4.0
5.0
6.0
Hours of Operation

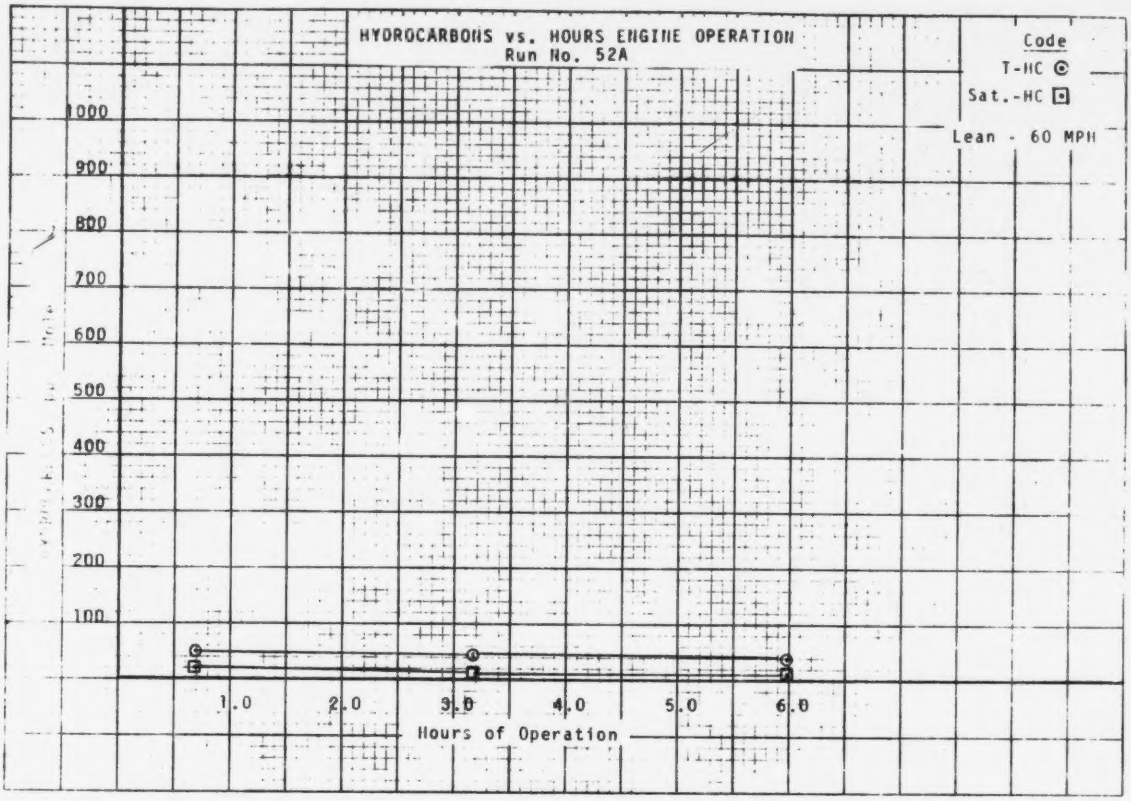

HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 43
Code
T-HC ⊙
Sat.-HC ⊡
HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
1.0
2.0
3.0
4.0
5.0
6.0
Hours of Operation

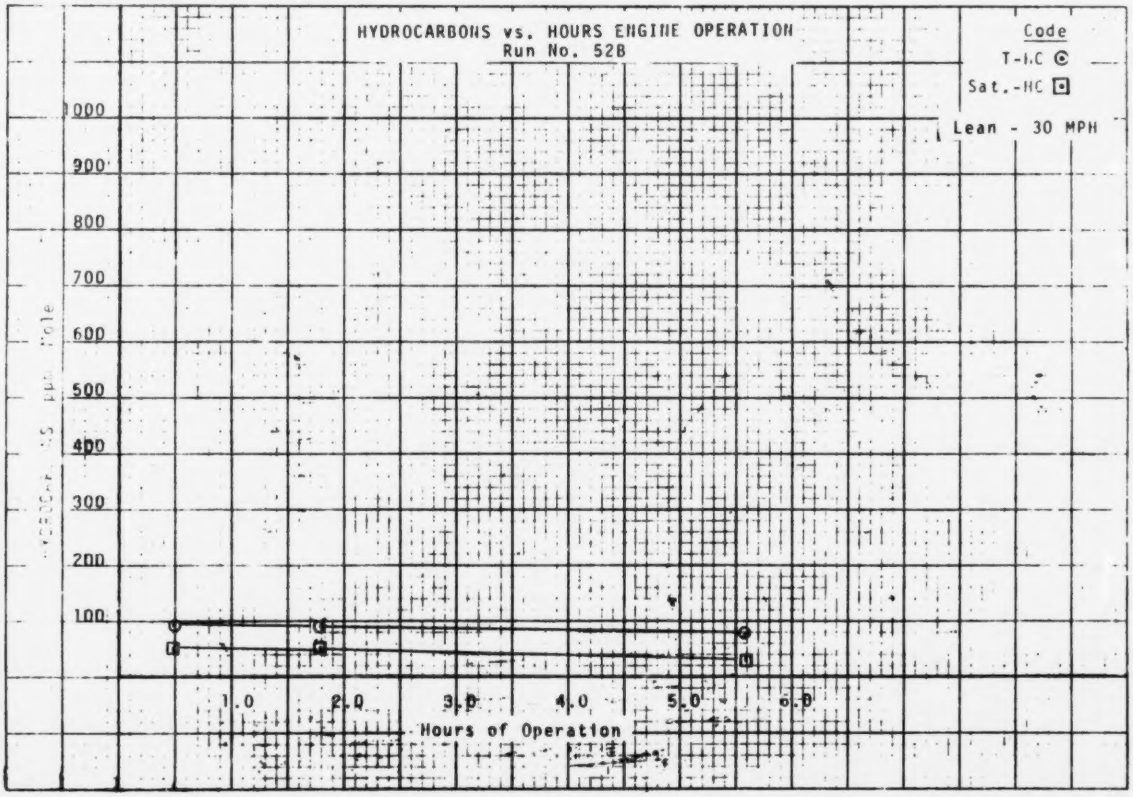

TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
Run No. 44

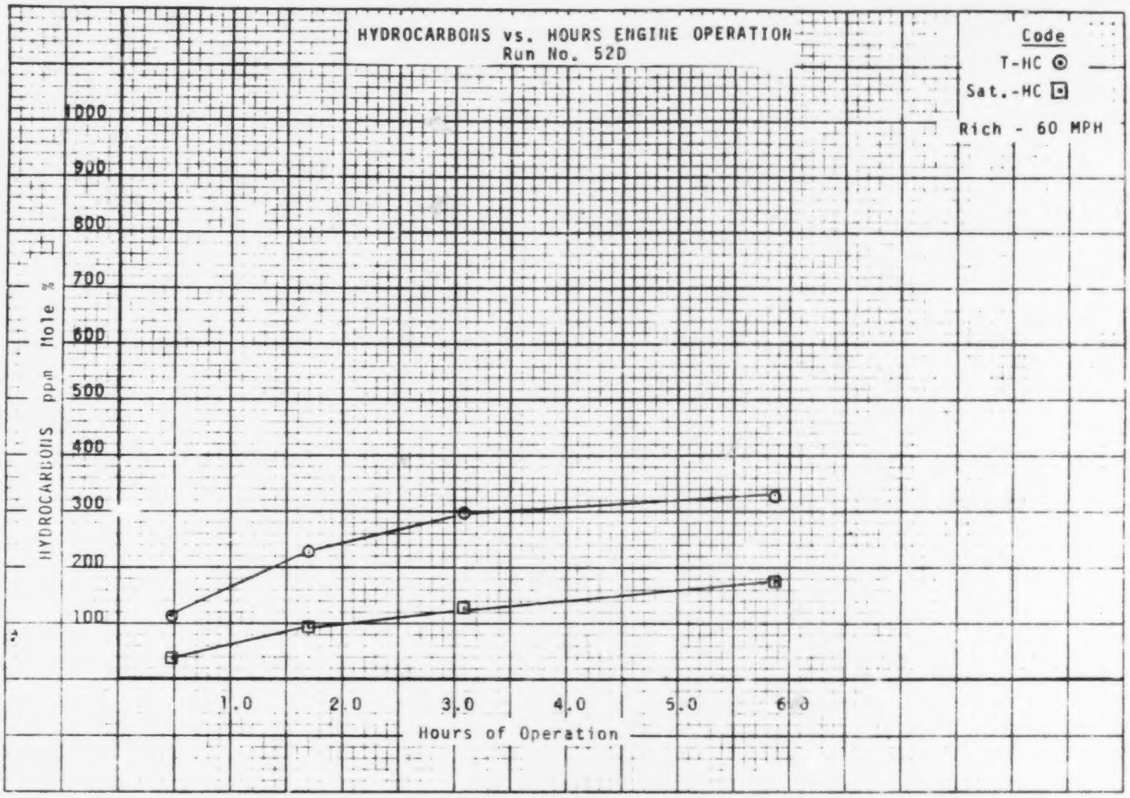

SATURATED HYDROCARBON vs. HOURS ENGINE OPERATION
Run No. 44

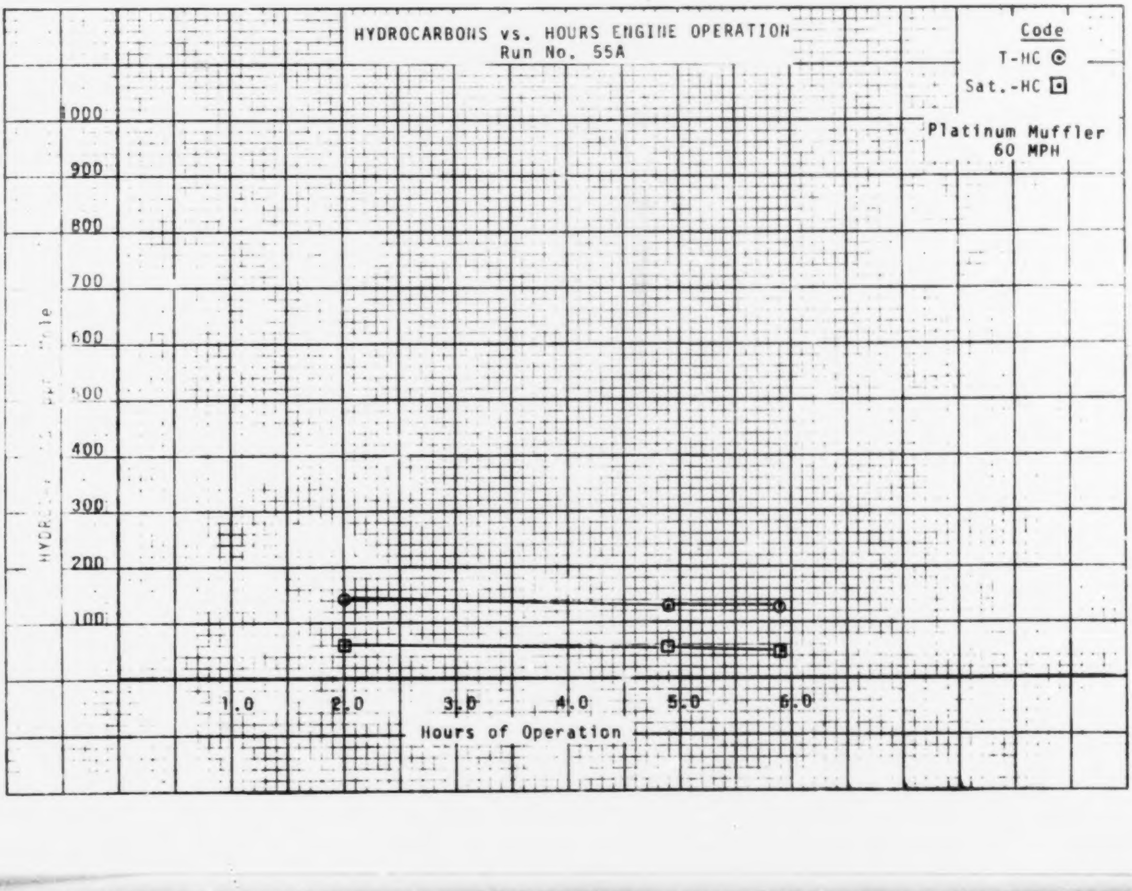

HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 45
Code
T-HC ⊙
Sat.-HC ⊡
HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
1.0
2.0
3.0
4.0
5.0
6.0
Hours of Operation

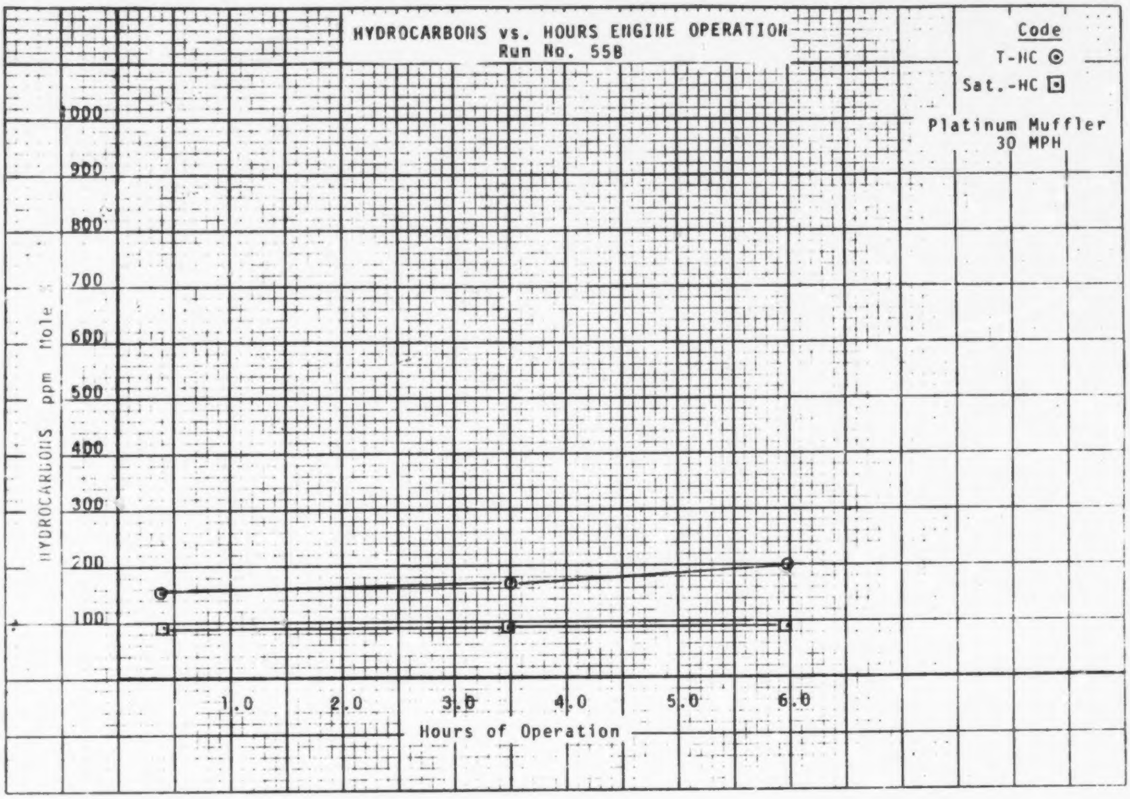

HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 50
Code
T-HC ⊙
Sat.-HC ⊡
HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
1.0
2.0
3.0
4.0
5.0
6.0
Hours of Operation

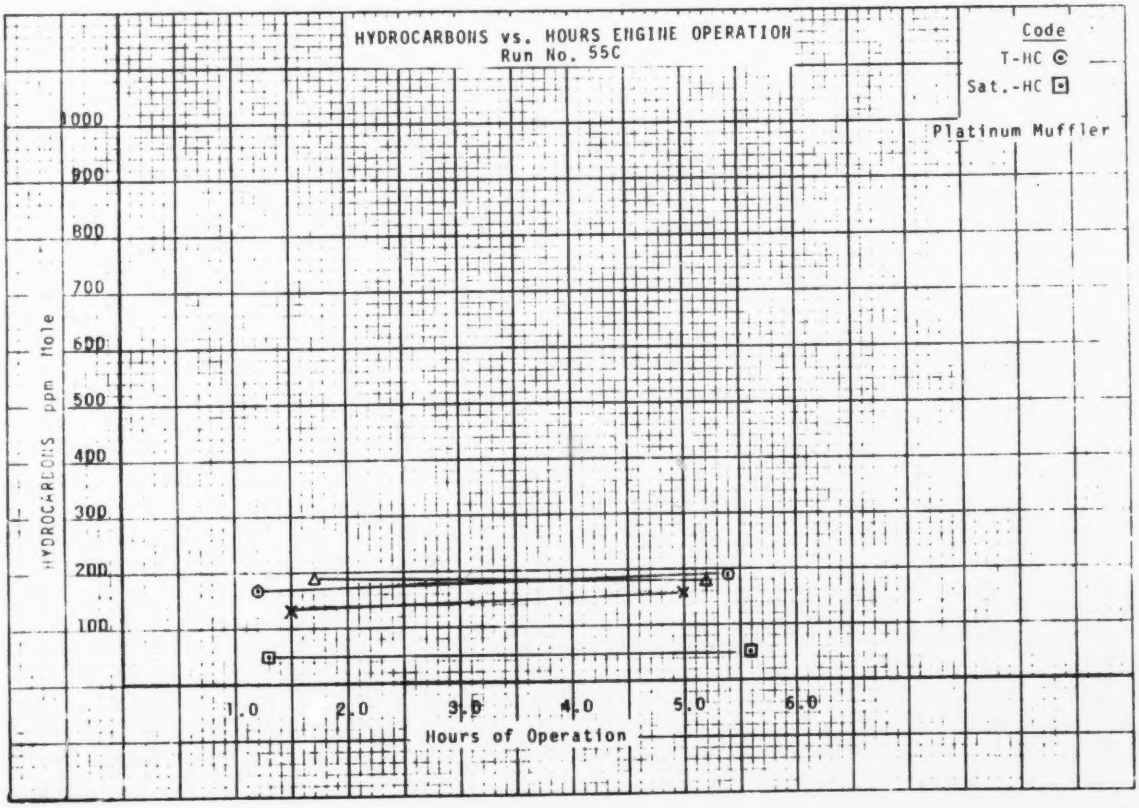

HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 52A

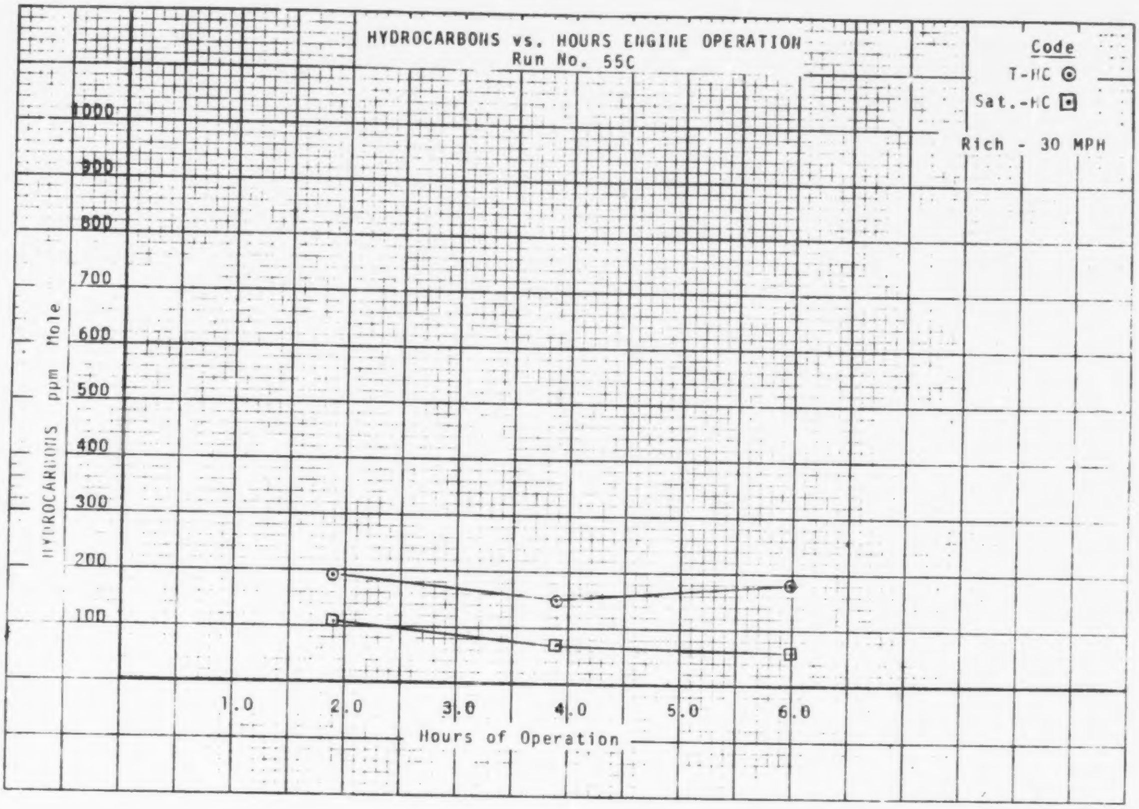

HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 52B

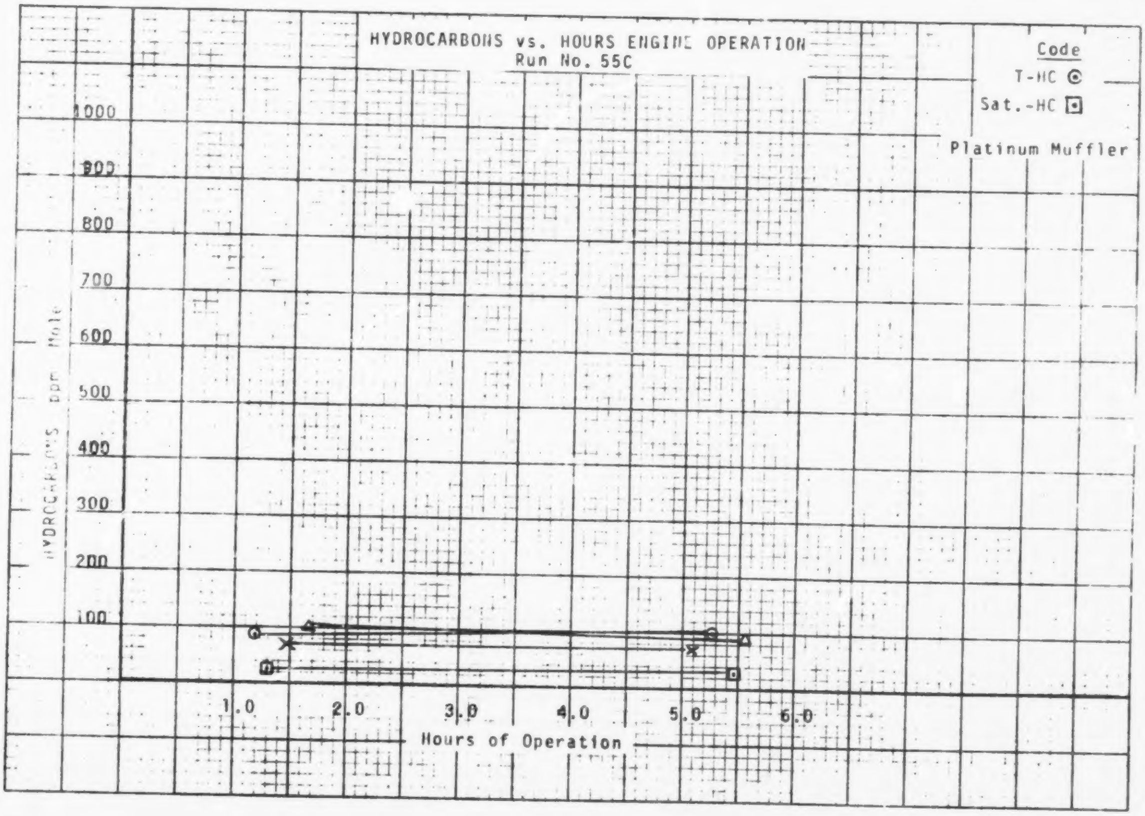

HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 52D
Code
T-HC ⊙
Sat.-HC ⊡
Rich - 60 MPH
HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
1.0
2.0
3.0
4.0
5.0
6.0
Hours of Operation

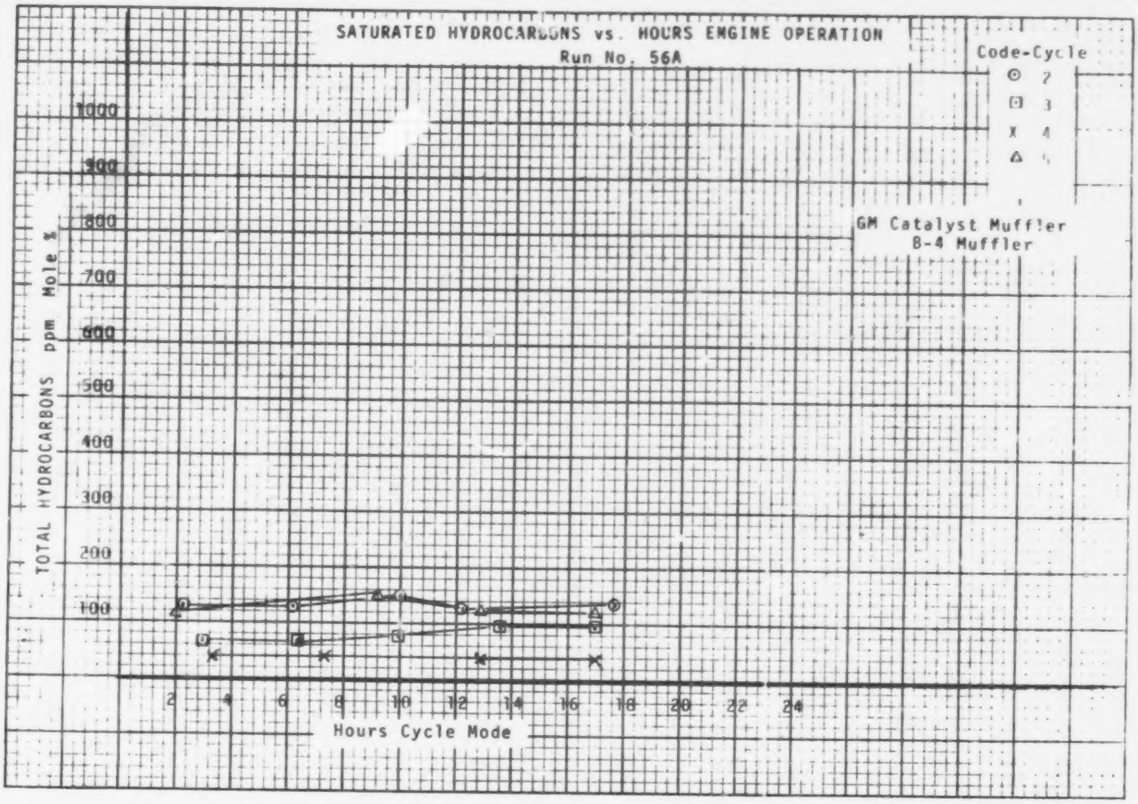

HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 55A
Code
T-HC ⊙
Sat.-HC ⊡
Platinum Muffler
60 MPH
1000
900
800
700
600
500
400
300
200
100
1.0
2.0
3.0
4.0
5.0
6.0
Hours of Operation

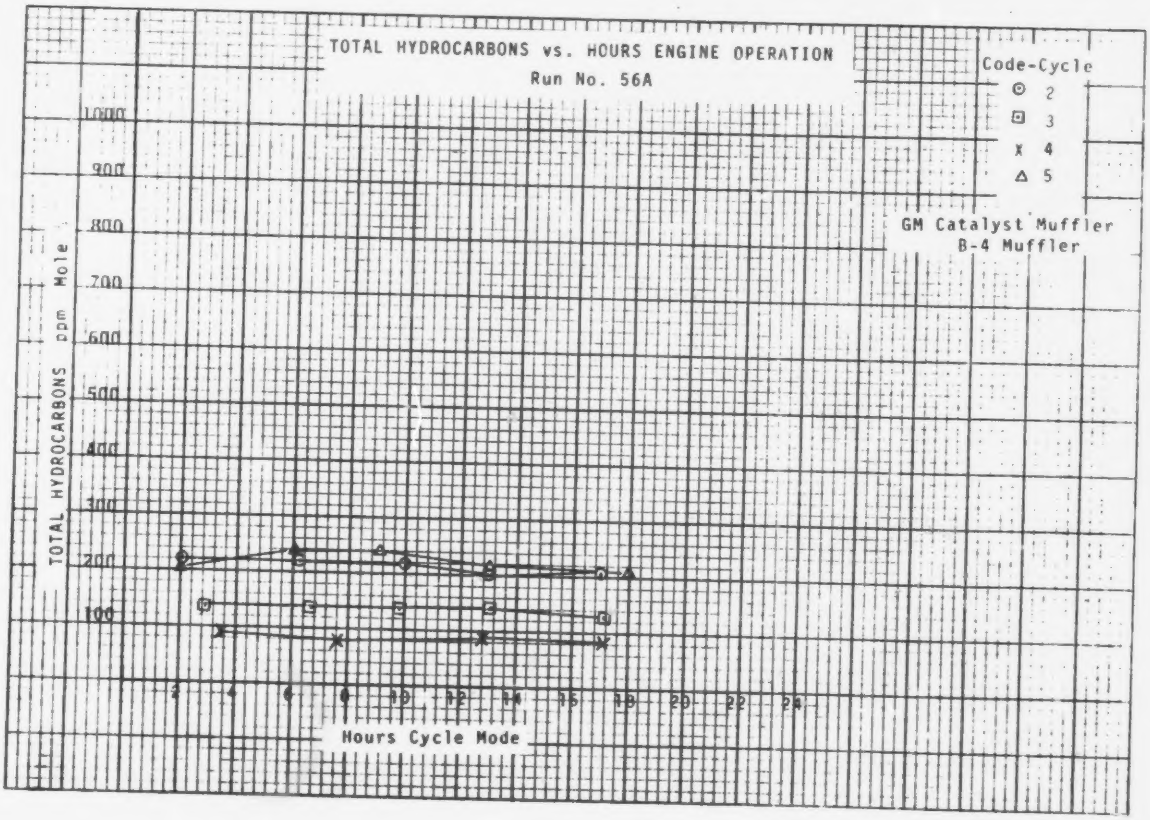

HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 55B
Code
T-HC ⊙
Sat.-HC ⊡
Platinum Muffler
30 MPH
HYDROCARBONS ppm Mole
1000
900
800
700
600
500
400
300
200
100
1.0
2.0
3.0
4.0
5.0
6.0
Hours of Operation

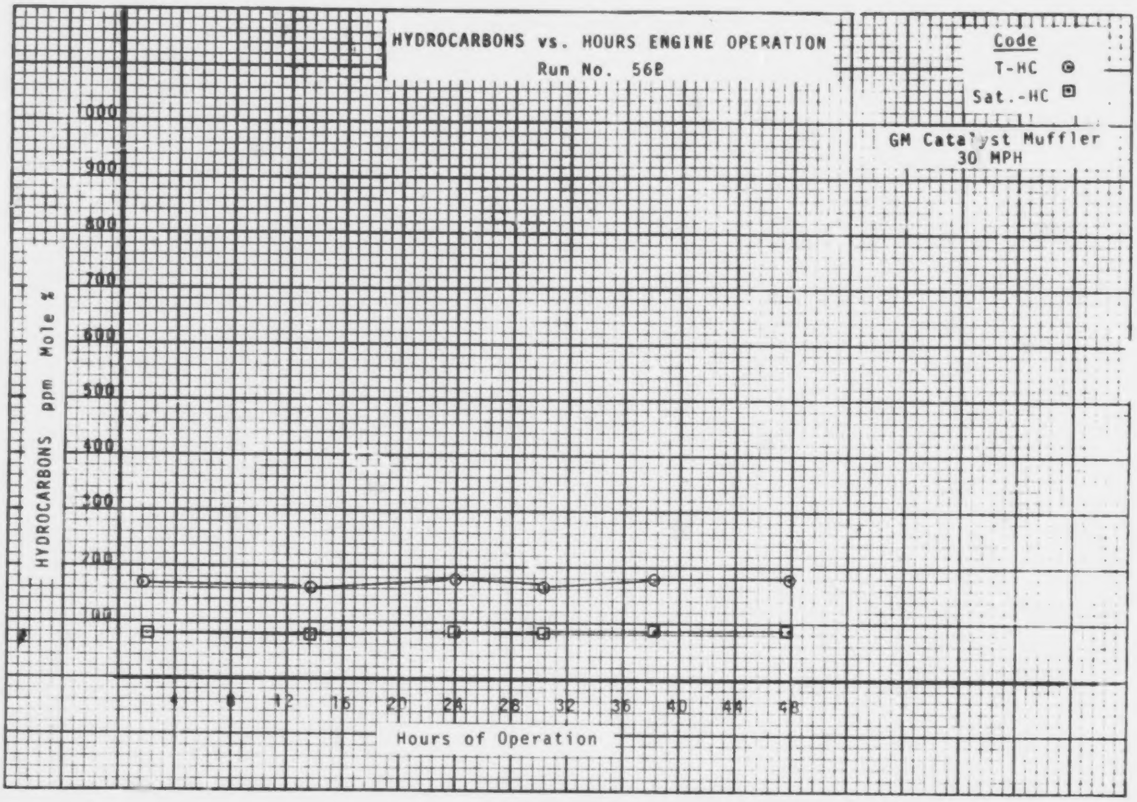

HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 55C
Code
T-HC ⊙
Sat.-HC ⊡
Platinum Muffler
HYDROCARBONS ppm Mole
1000
900
800
700
600
500
400
300
200
100
1.0
2.0
3.0
4.0
5.0
6.0
Hours of Operation

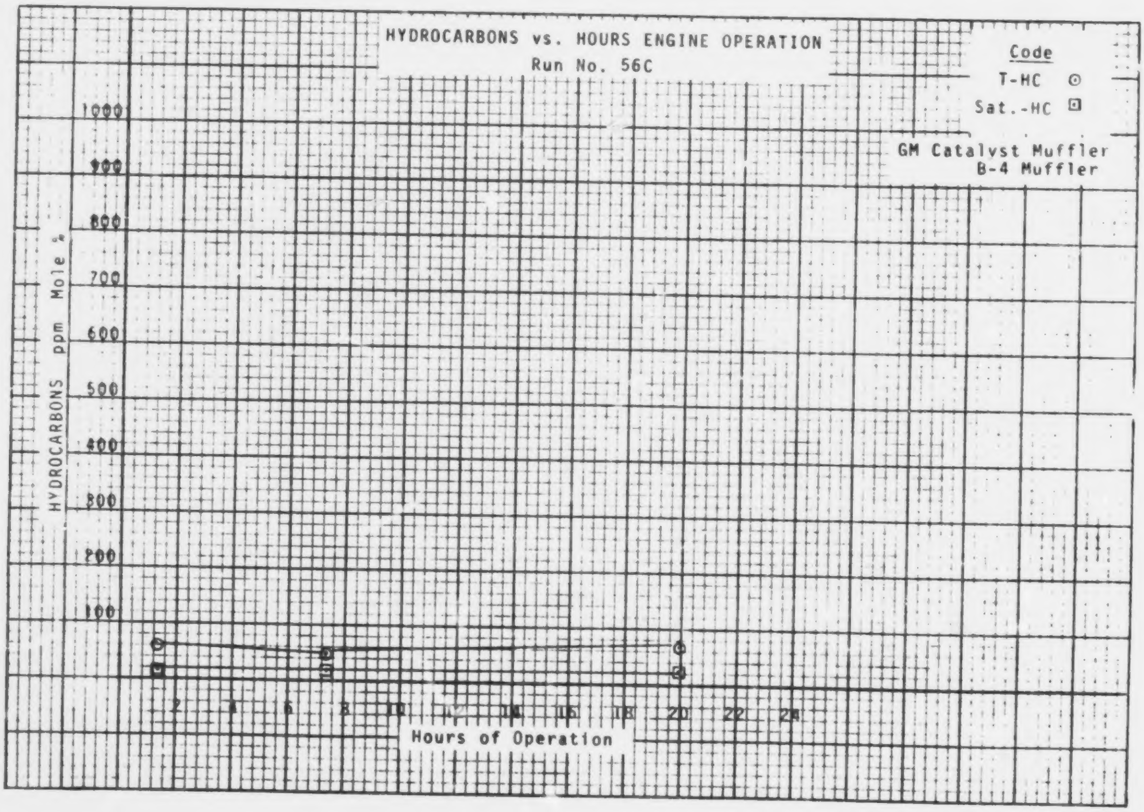

HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 55C
Code
T-HC ⊙
Sat.-HC ⊡
Rich - 30 MPH
HYDROCARBONS ppm Mole
1000
900
800
700
600
500
400
300
200
100
1.0
2.0
3.0
4.0
5.0
6.0
Hours of Operation

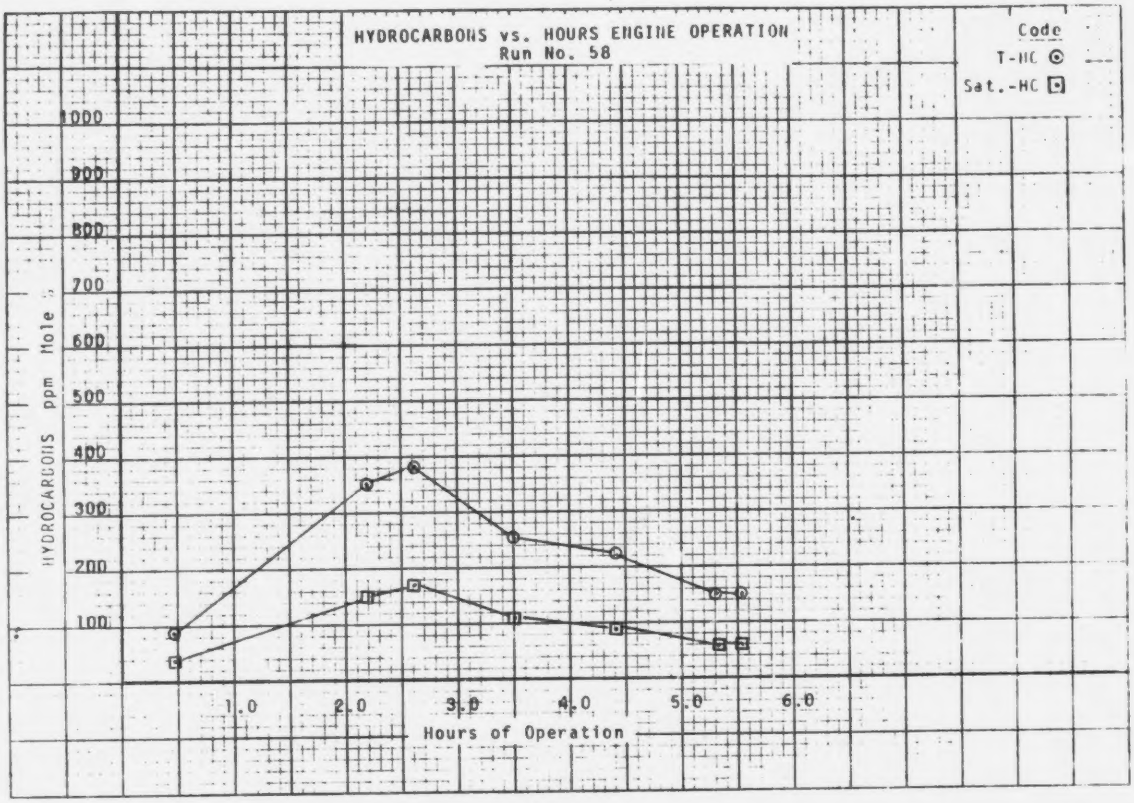

HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 55C
Code
T-HC ⊙
Sat.-HC ⊡
Platinum Muffler
HYDROCARBONS ppm Mole
1000
900
800
700
600
500
400
300
200
100
1.0
2.0
3.0
4.0
5.0
6.0
Hours of Operation

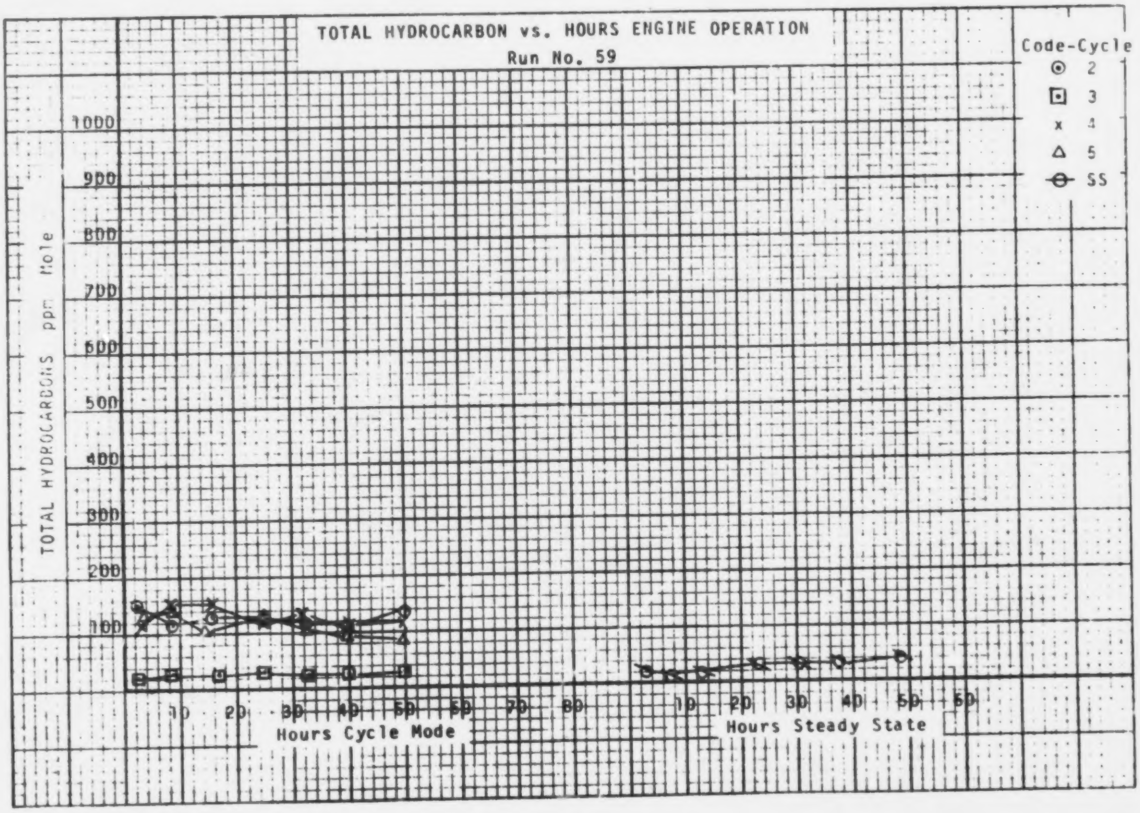

SATURATED HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 56A
Code-Cycle
⊙ 2
⊡ 3
X 4
△ 5
GM Catalyst Muffler
B-4 Muffler
TOTAL HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
2
4
6
8
10
12
14
16
18
20
22
24
Hours Cycle Mode

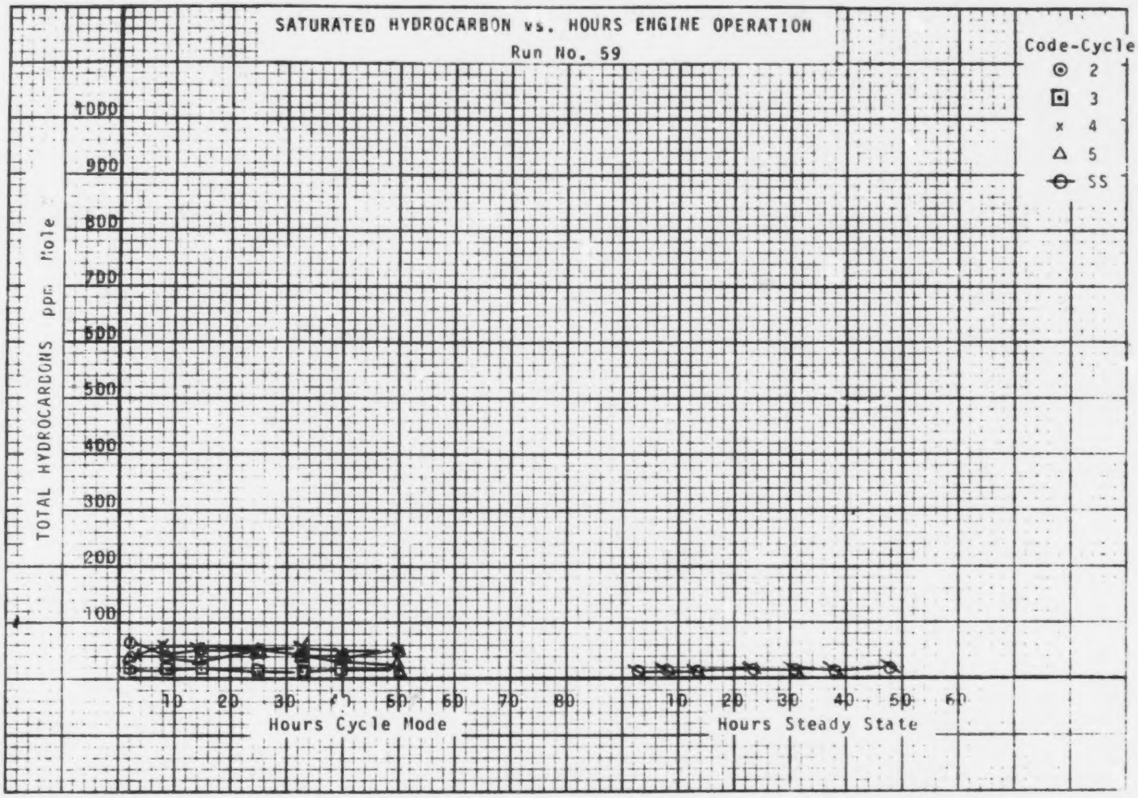

TOTAL HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 56A
Code-Cycle
⊙ 2
⊡ 3
X 4
△ 5
GM Catalyst Muffler
B-4 Muffler
TOTAL HYDROCARBONS ppm Mole
1000
900
800
700
600
500
400
300
200
100
2
4
6
8
10
12
14
16
18
20
22
24
Hours Cycle Mode

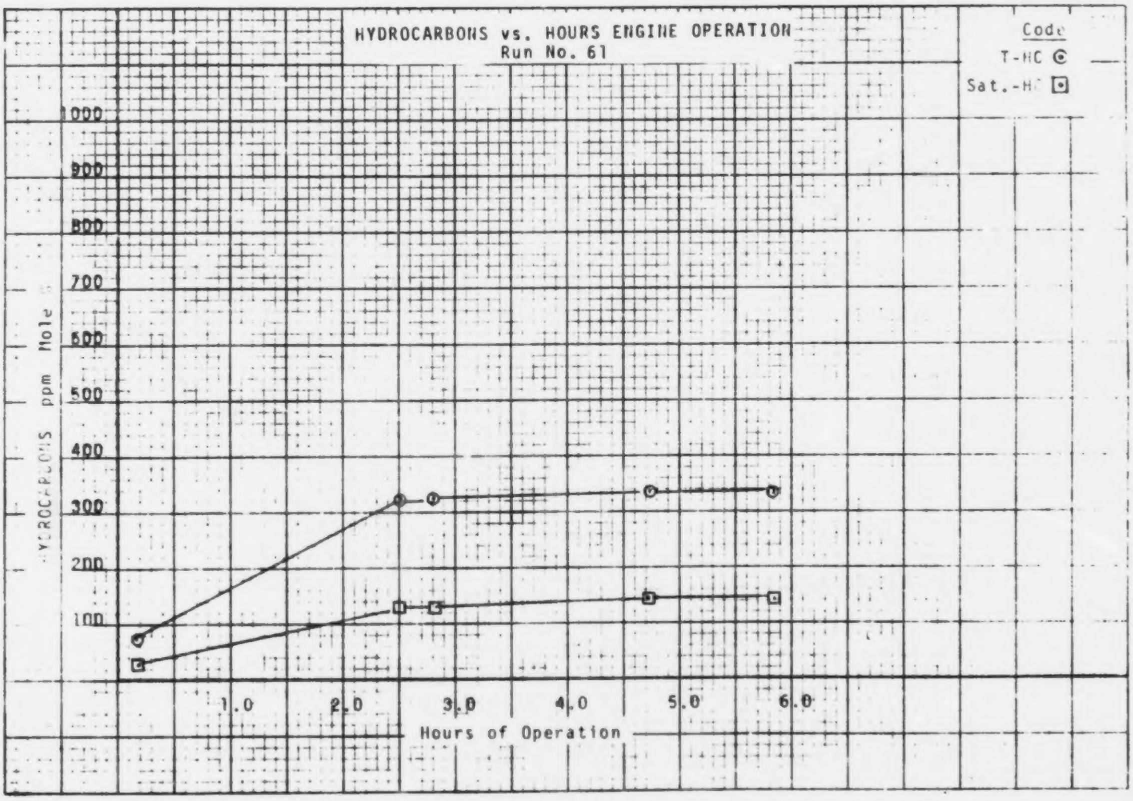

HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 56B
Code
T-HC ⊙
Sat.-HC ⊡
GM Catalyst Muffler
30 MPH
HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
4
8
12
16
20
24
28
32
36
40
44
48
Hours of Operation

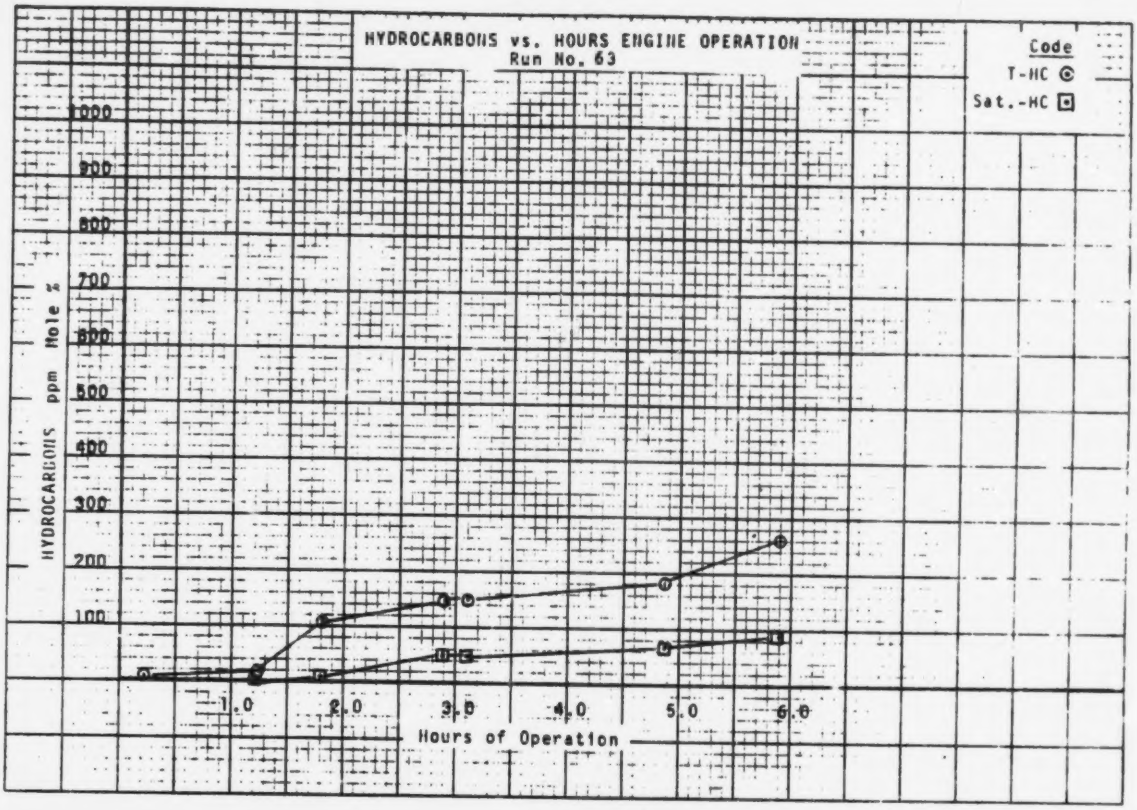

HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 56C
Code
T-HC ⊙
Sat.-HC ⊡
GM Catalyst Muffler
B-4 Muffler
HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
2
4
6
8
10
12
14
16
18
20
22
24
Hours of Operation

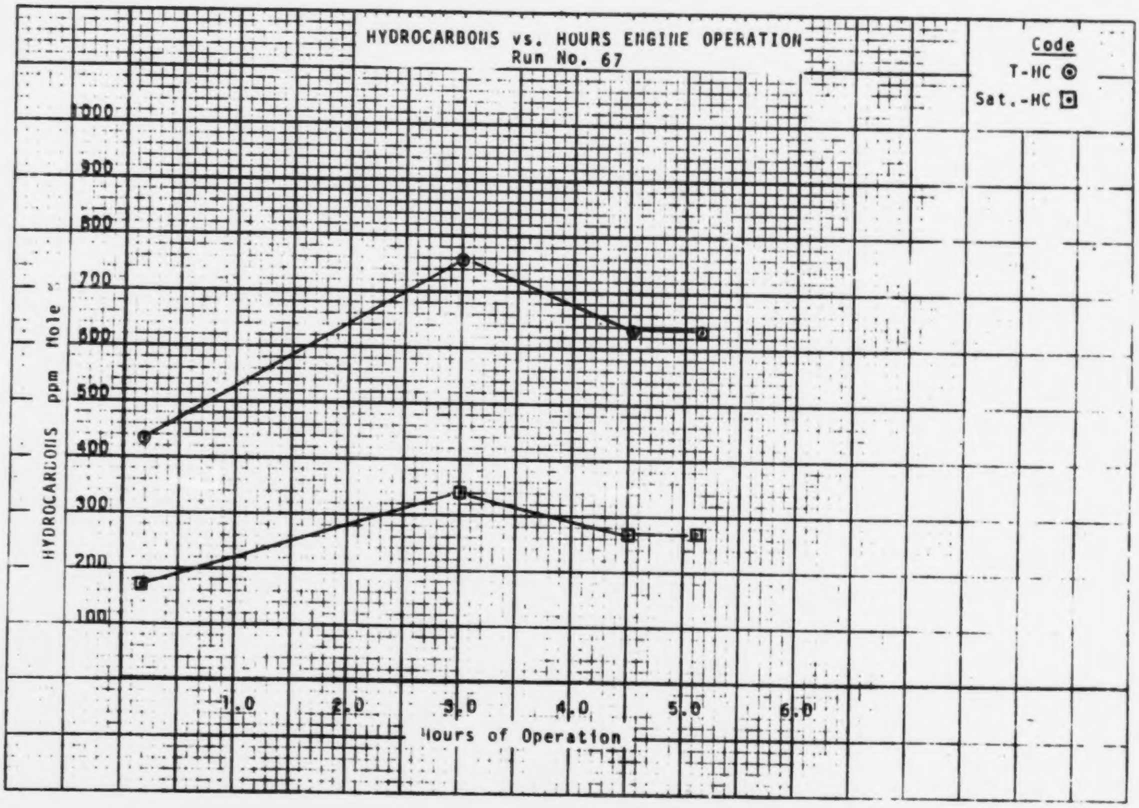

HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 58
Code
T-HC ⊙
Sat.-HC ⊡
1000
900
800
700
600
500
400
300
200
100
HYDROCARBONS ppm Mole %
1.0
2.0
3.0
4.0
5.0
6.0
Hours of Operation


TOTAL HYDROCARBON vs. HOURS ENGINE OPERATION
Run No. 59
Code-Cycle
⊙ 2
⊡ 3
x 4
△ 5
SS
1000
900
800
700
600
500
400
300
200
100
TOTAL HYDROCARBONS ppm Mole
10
20
30
40
50
60
70
80
Hours Cycle Mode
10
20
30
40
50
60
Hours Steady State


SATURATED HYDROCARBON vs. HOURS ENGINE OPERATION
Run No. 59
Code-Cycle
⊙ 2
⊡ 3
x 4
△ 5
-⊖- SS
TOTAL HYDROCARBONS ppm Mole
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
10
20
30
40
50
60
Hours Cycle Mode
Hours Steady State

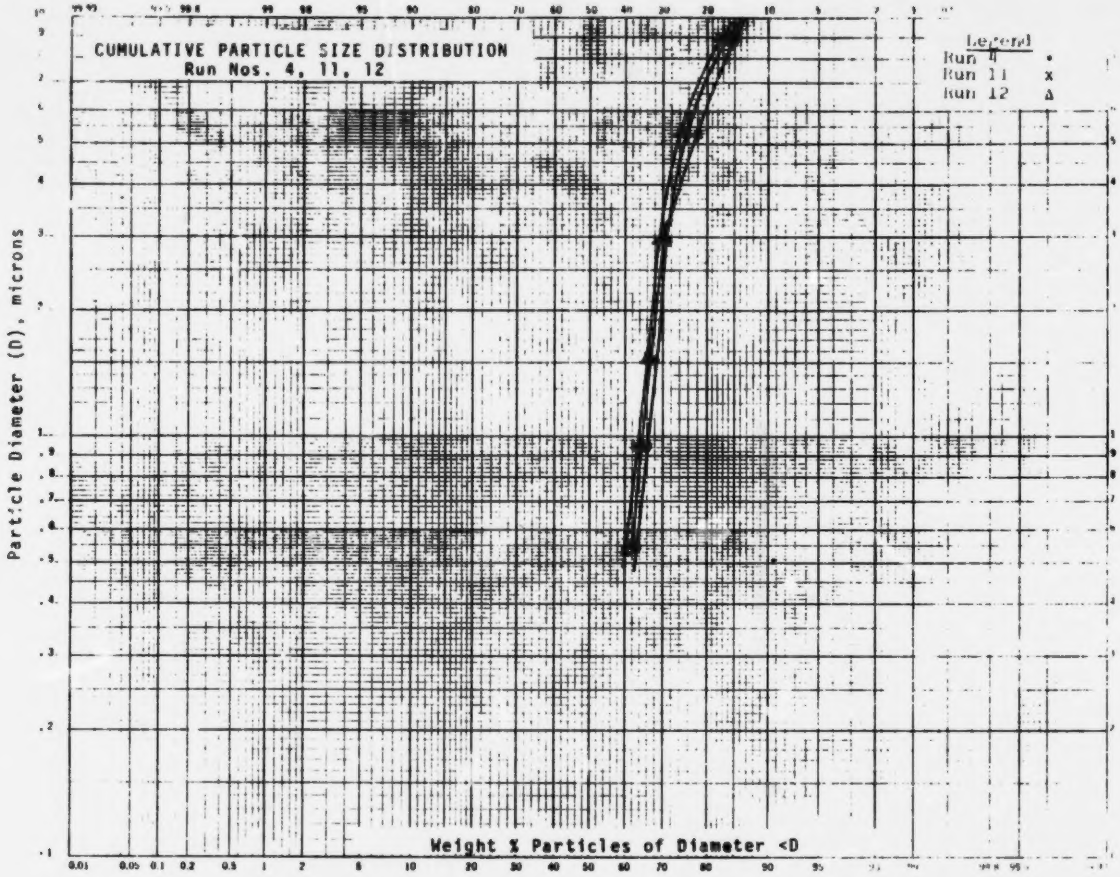

HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 61
Code
T-HC ⊙
Sat.-HC ⊡
HYDROCARBONS ppm Mole
1000
900
800
700
600
500
400
300
200
100
1.0
2.0
3.0
4.0
5.0
6.0
Hours of Operation

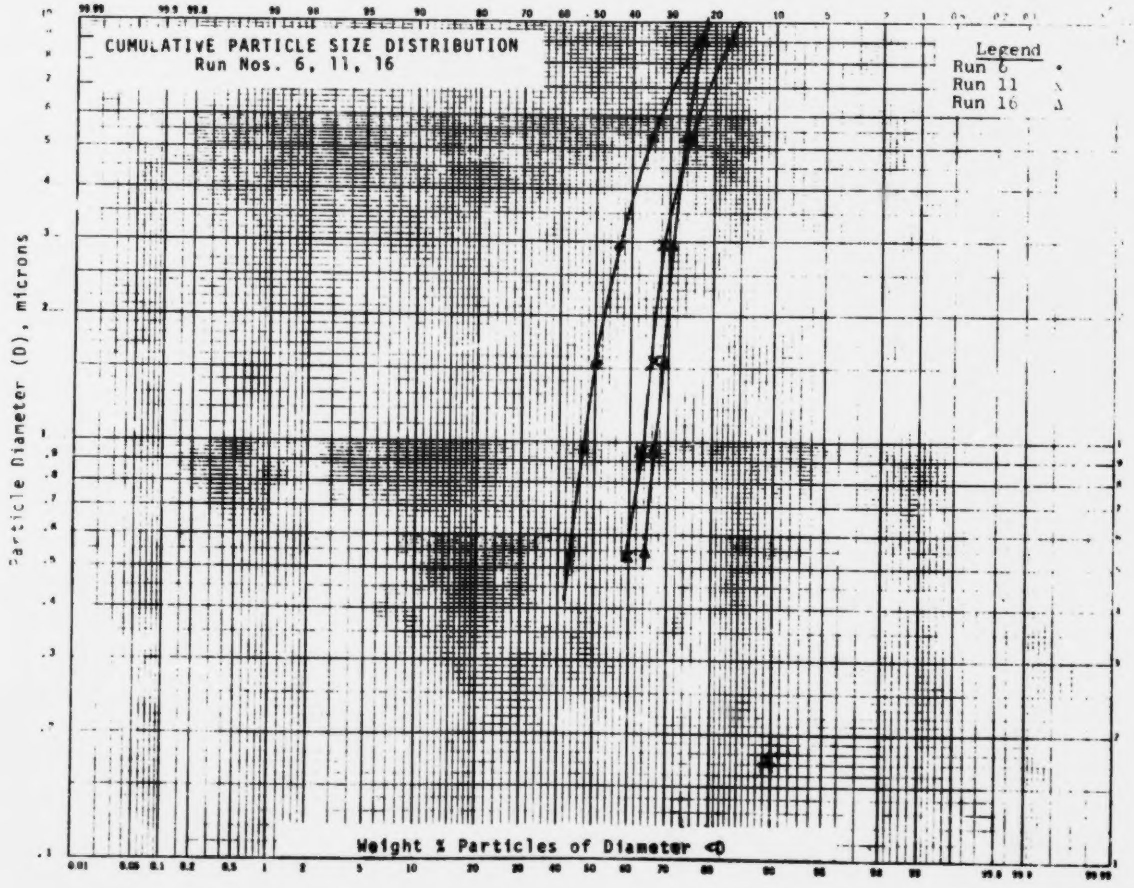

HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 63
Code
T-HC ⊙
Sat.-HC ⊡
HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
1.0
2.0
3.0
4.0
5.0
6.0
Hours of Operation

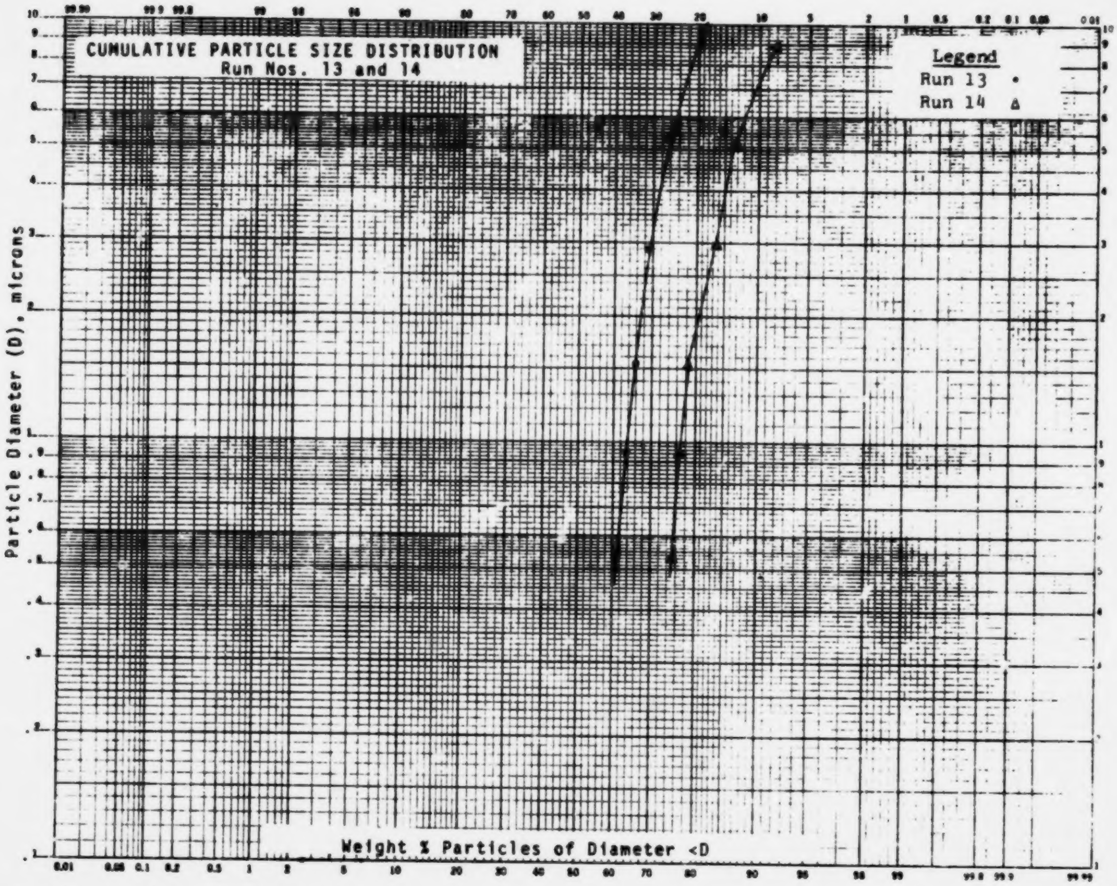

HYDROCARBONS vs. HOURS ENGINE OPERATION
Run No. 67
Code
T-HC ⊙
Sat.-HC ⊡
HYDROCARBONS ppm Mole %
1000
900
800
700
600
500
400
300
200
100
1.0
2.0
3.0
4.0
5.0
6.0
Hours of Operation

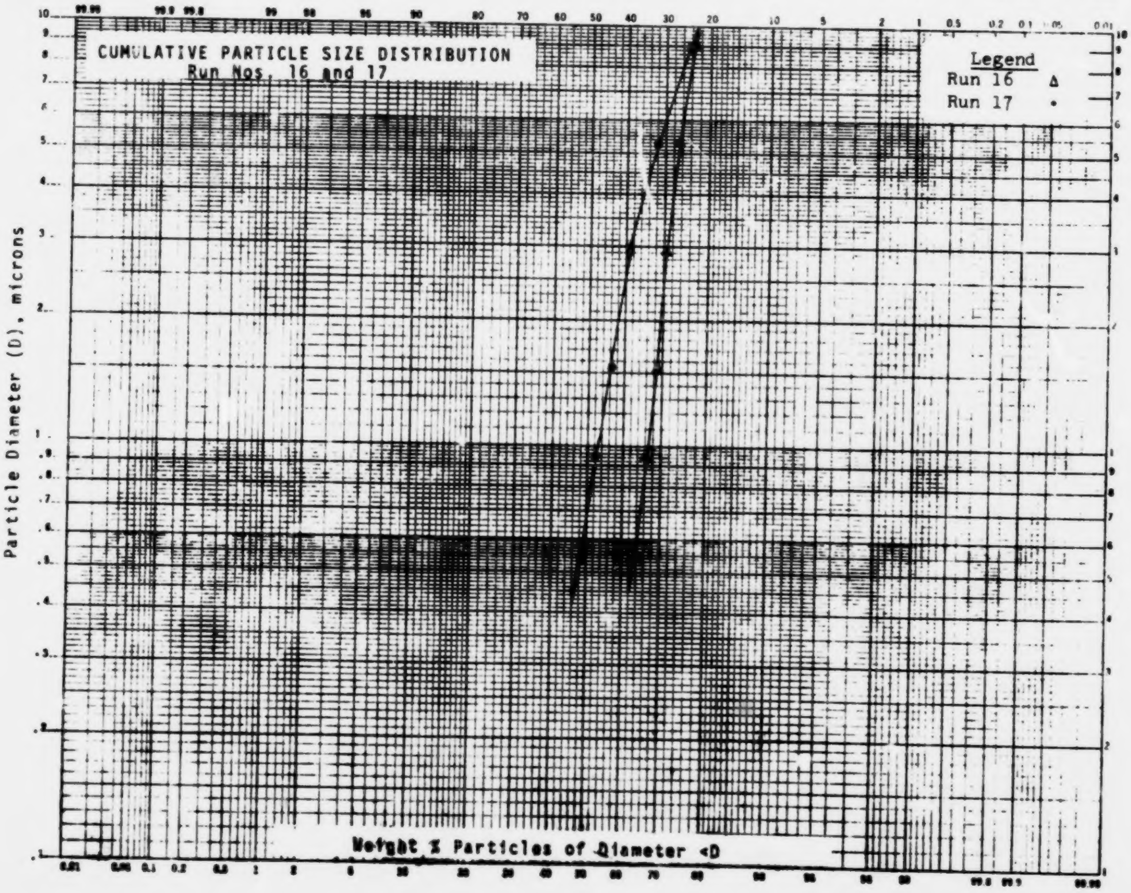
APPENDIX B

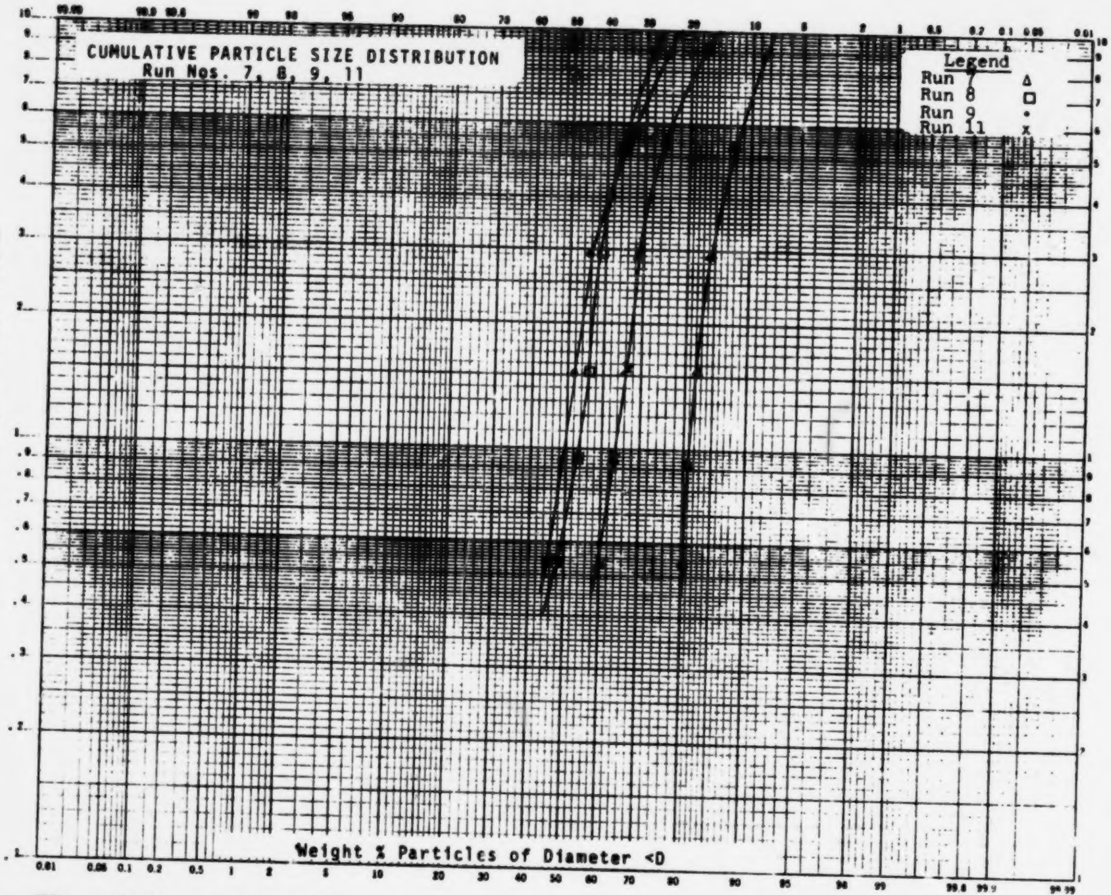
Cumulative Mass Distribution for Collected Exhaust Particles by Run Number

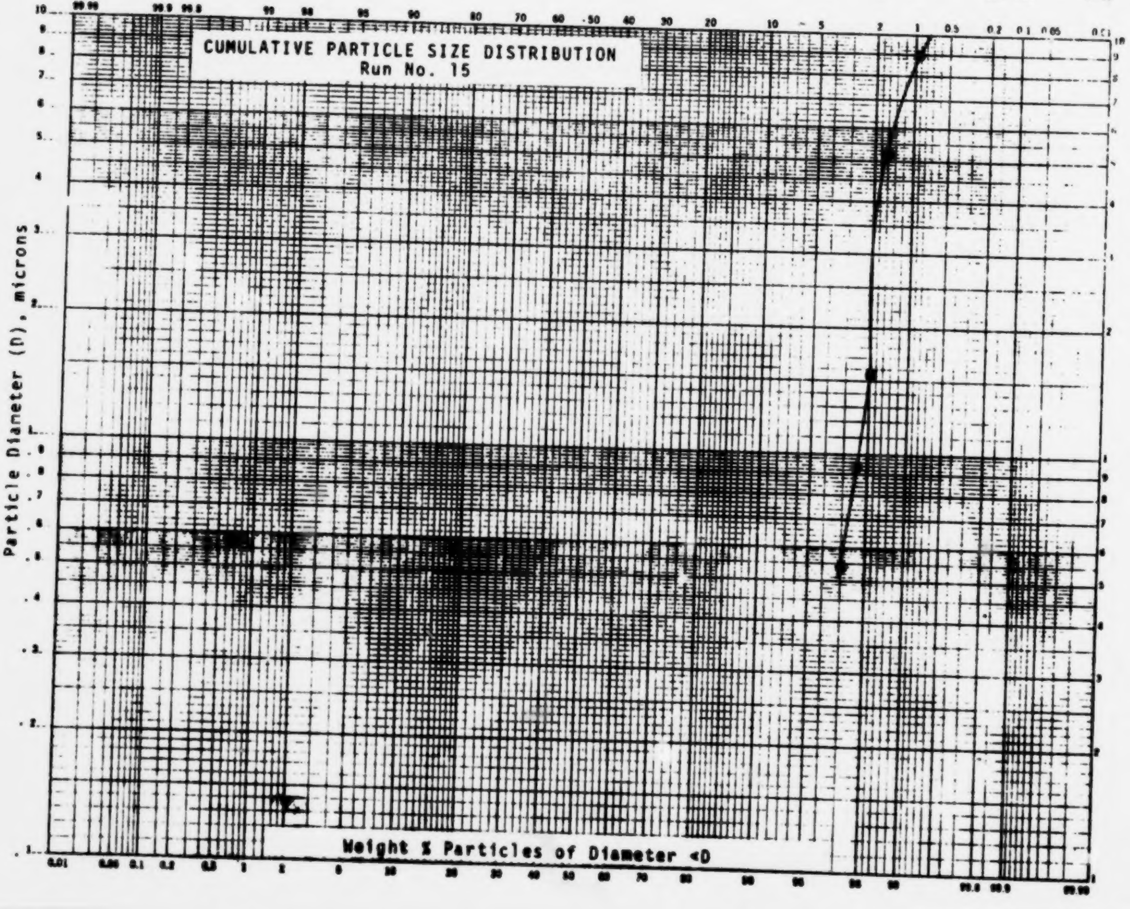

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run Nos. 4, 11, 12
Legend
Run 4 •
Run 11 x
Run 12 Δ
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
99
98
95
90
80
70
60
50
40
30
20
10
5
2
1
.1
.2
.3
.4
.5
.6
.7
.8
.9
1
2
3
4
5
6
7
9
10

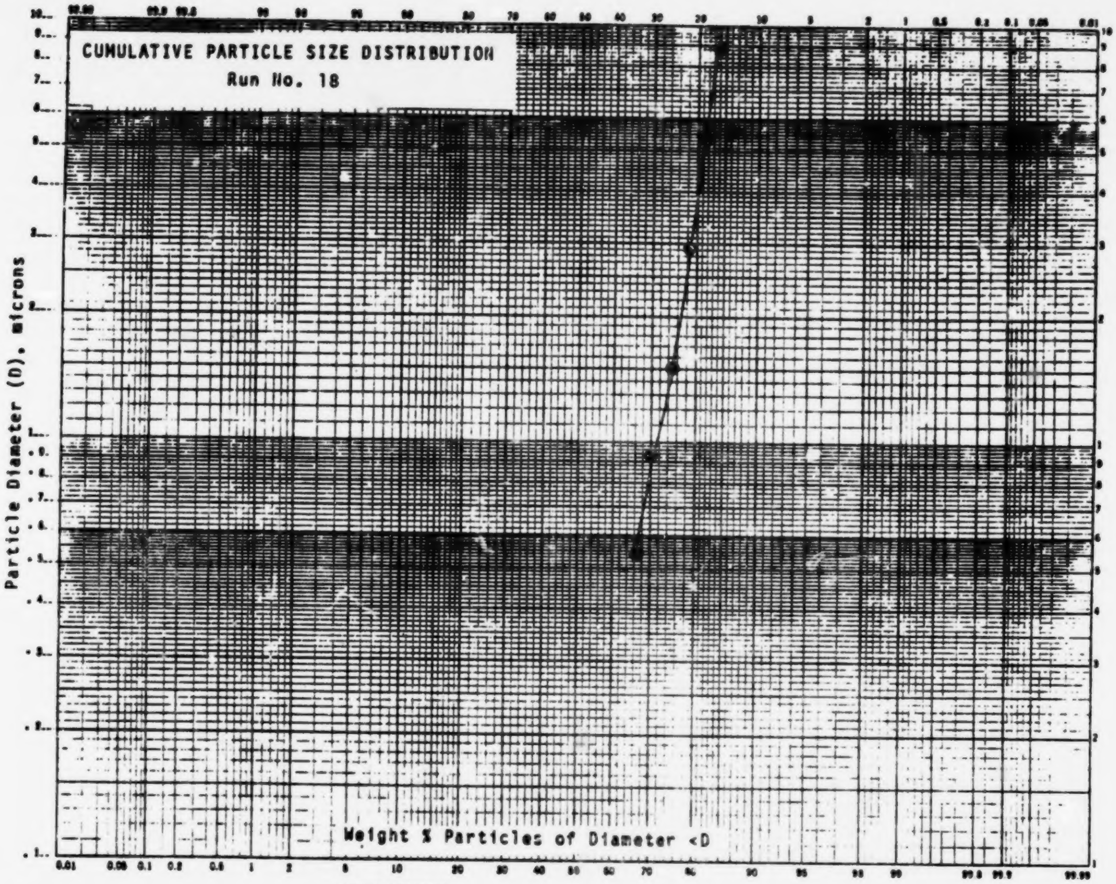

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run Nos. 6, 11, 16
Legend
Run 6 •
Run 11 x
Run 16 Δ
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
99.99
99.9
99.8
99
98
95
90
80
70
60
50
40
30
20
10
5
2
1
.1
.3
.4
.5
.6
.7
.8
.9
1
2
3
4
5
6
7
10

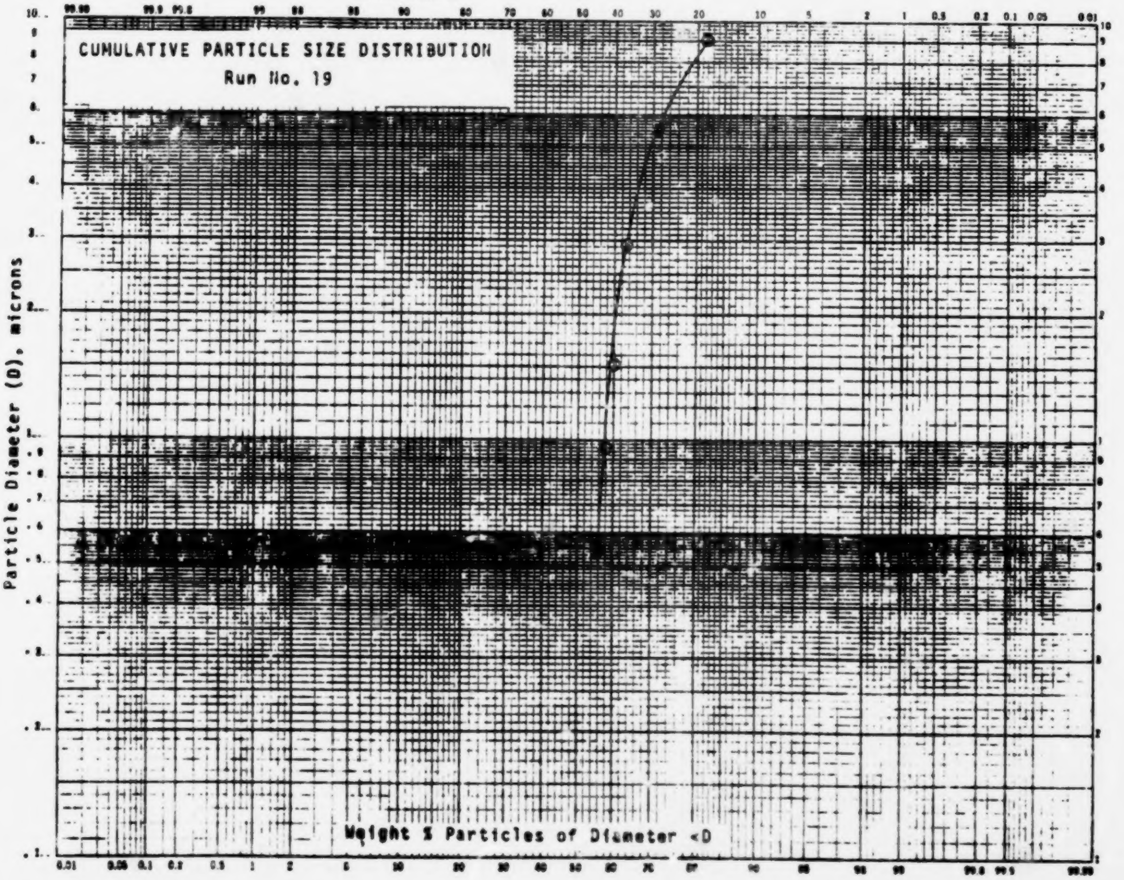

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run Nos. 13 and 14
Legend
Run 13 •
Run 14 Δ
Particle Diameter (D), microns
Weight % Particles of Diameter <D

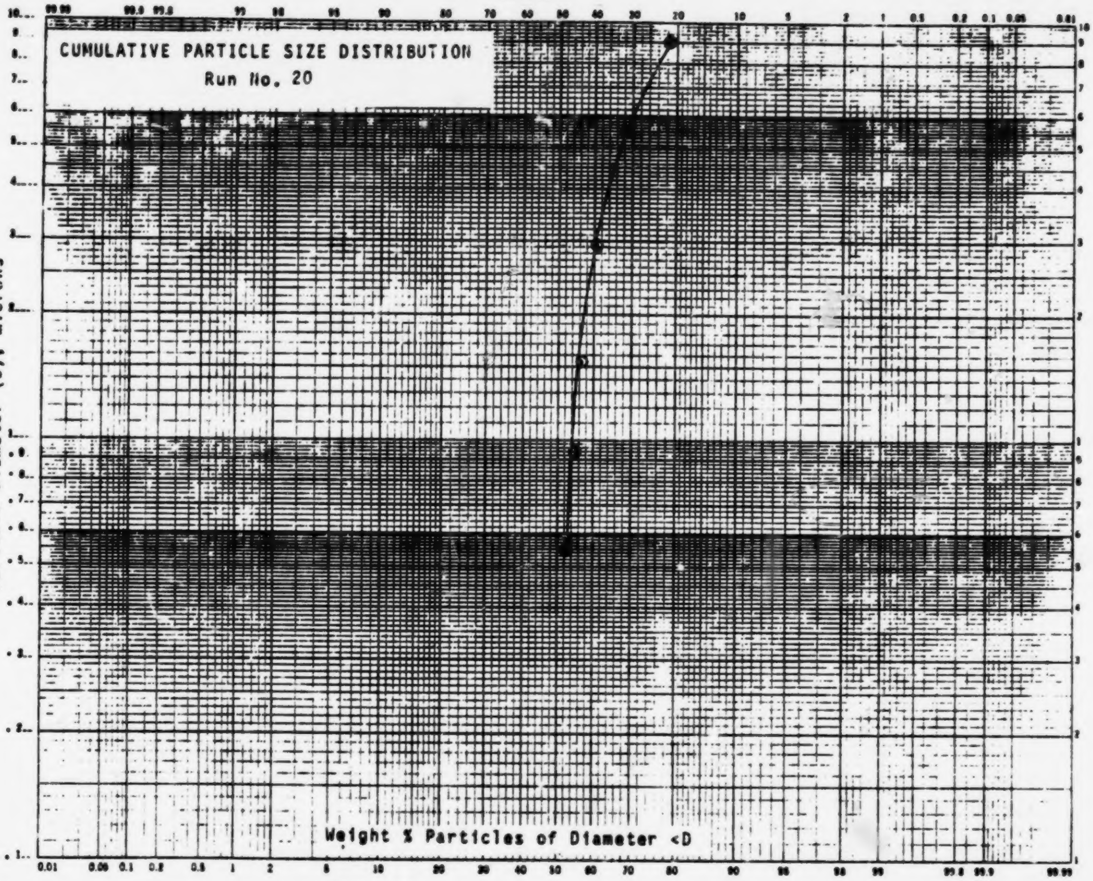

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run Nos. 16 and 17
Legend
Run 16 Δ
Run 17 •
Particle Diameter (D), microns
Weight % Particles of Diameter <D


CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run Nos. 7, 8, 9, 11
Legend
Run 7 Δ
Run 8 □
Run 9 •
Run 11 x
Particle Diameter (D), microns
Weight % Particles of Diameter <D

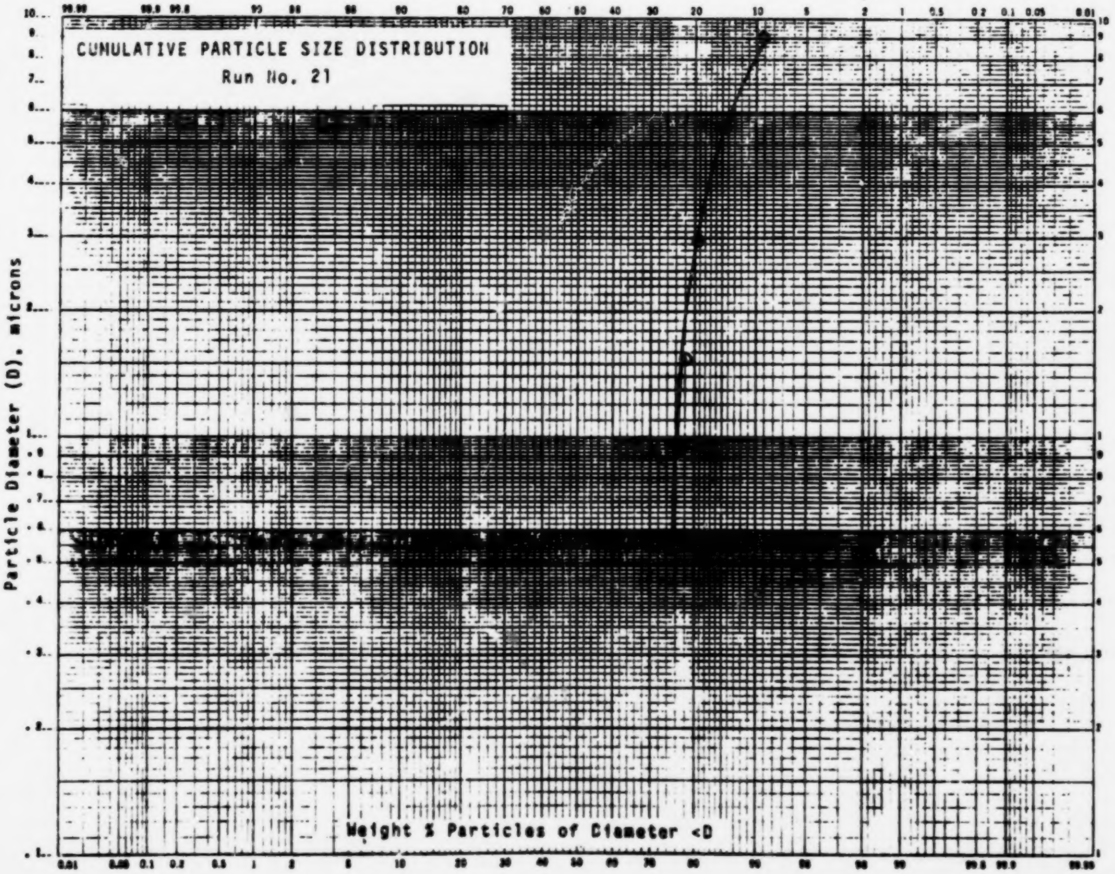

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 15
Particle Diameter (D), microns
Weight % Particles of Diameter <D


CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 18
Particle Diameter (D), microns
Weight % Particles of Diameter <D
99.99
99.9
99.8
99
98
95
90
80
70
60
50
40
30
20
10
5
2
1
0.5
0.2
0.1
0.05
0.01

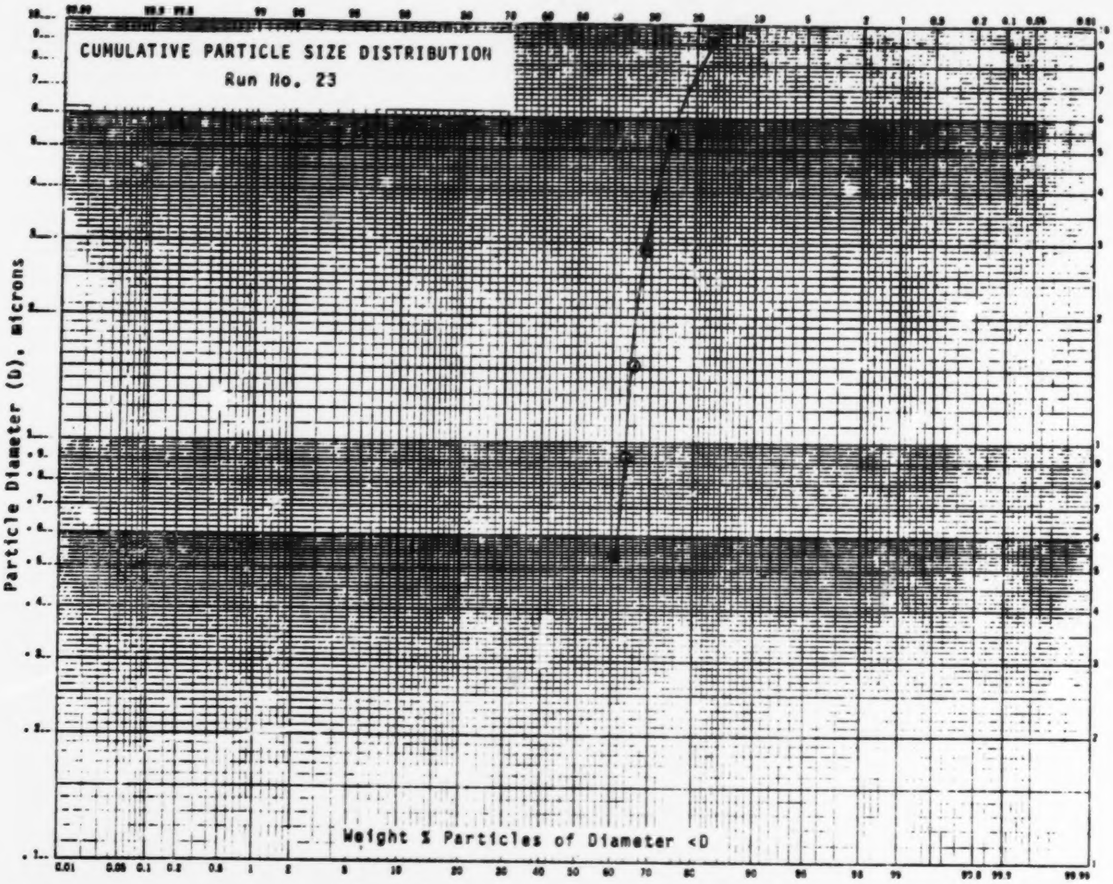

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 19
Particle Diameter (D), microns
Weight % Particles of Diameter <D
99.99
99.9
99.8
99
98
95
90
80
70
60
50
40
30
20
10
5
2
1
0.5
0.2
0.1
0.05
0.01

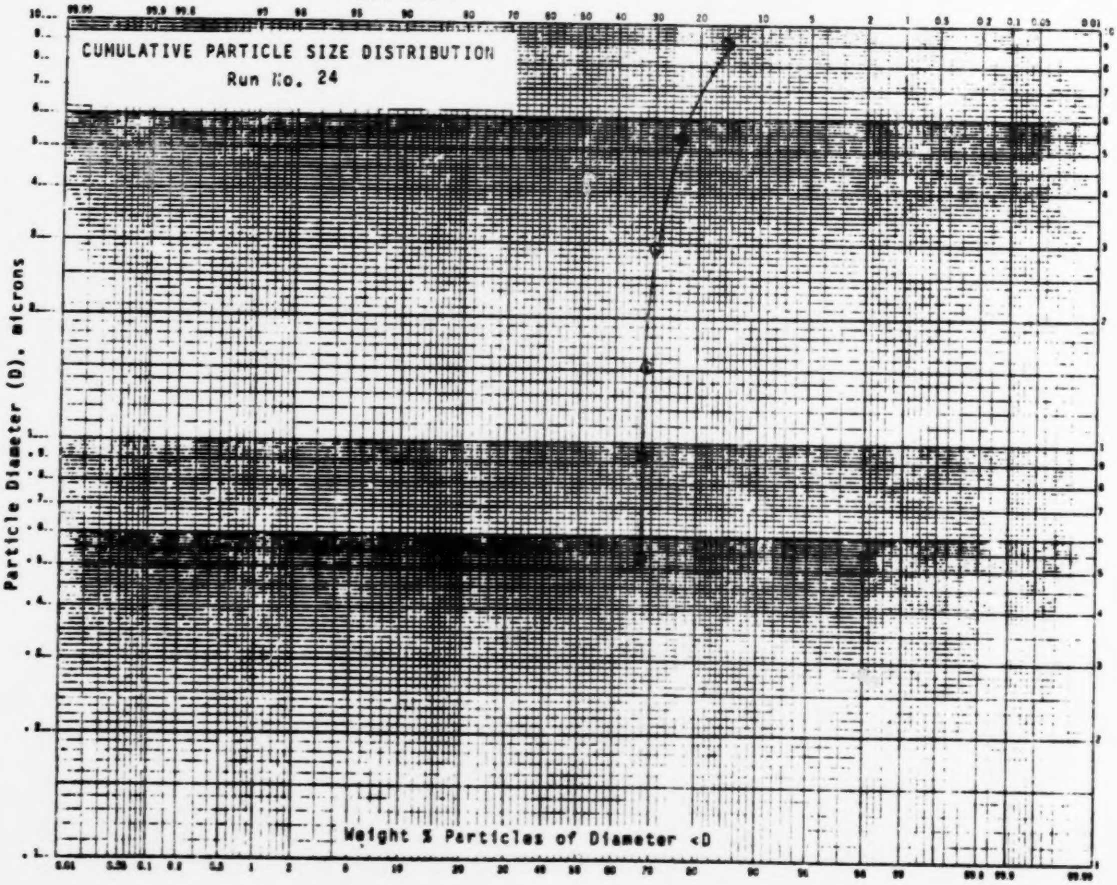


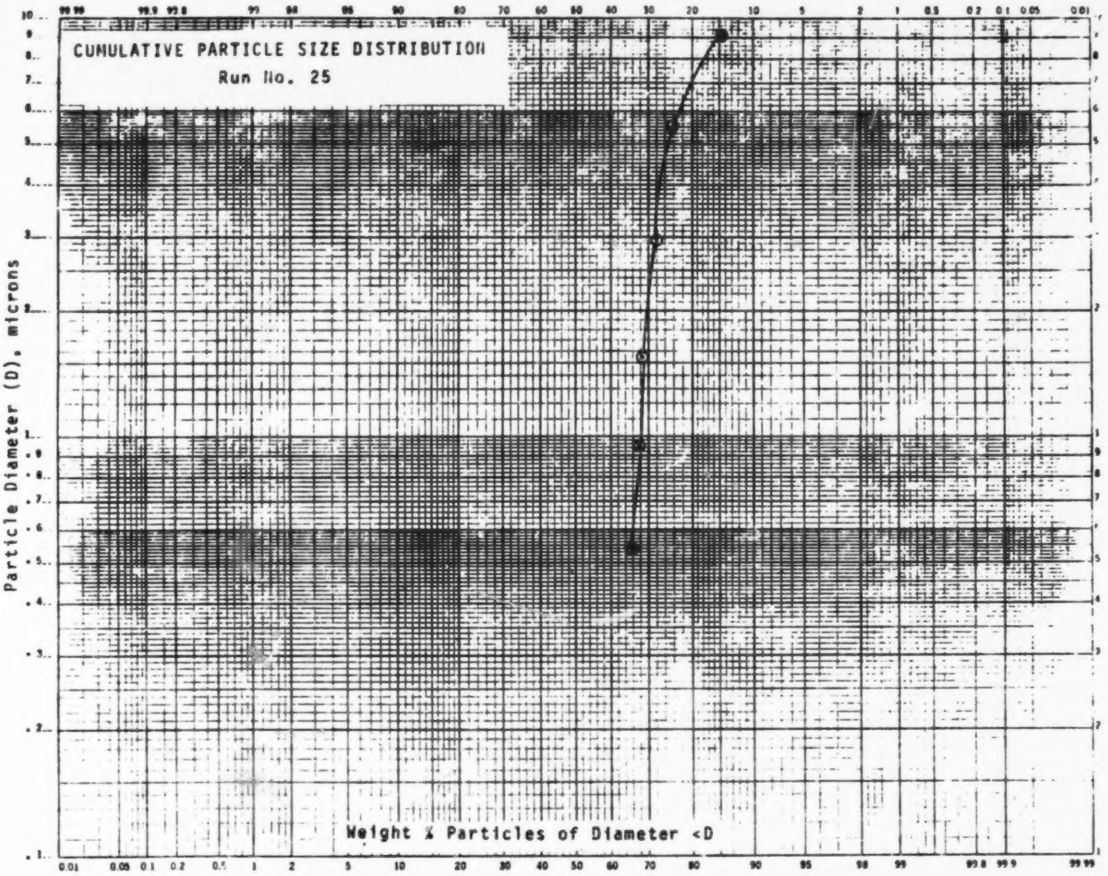
CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 20



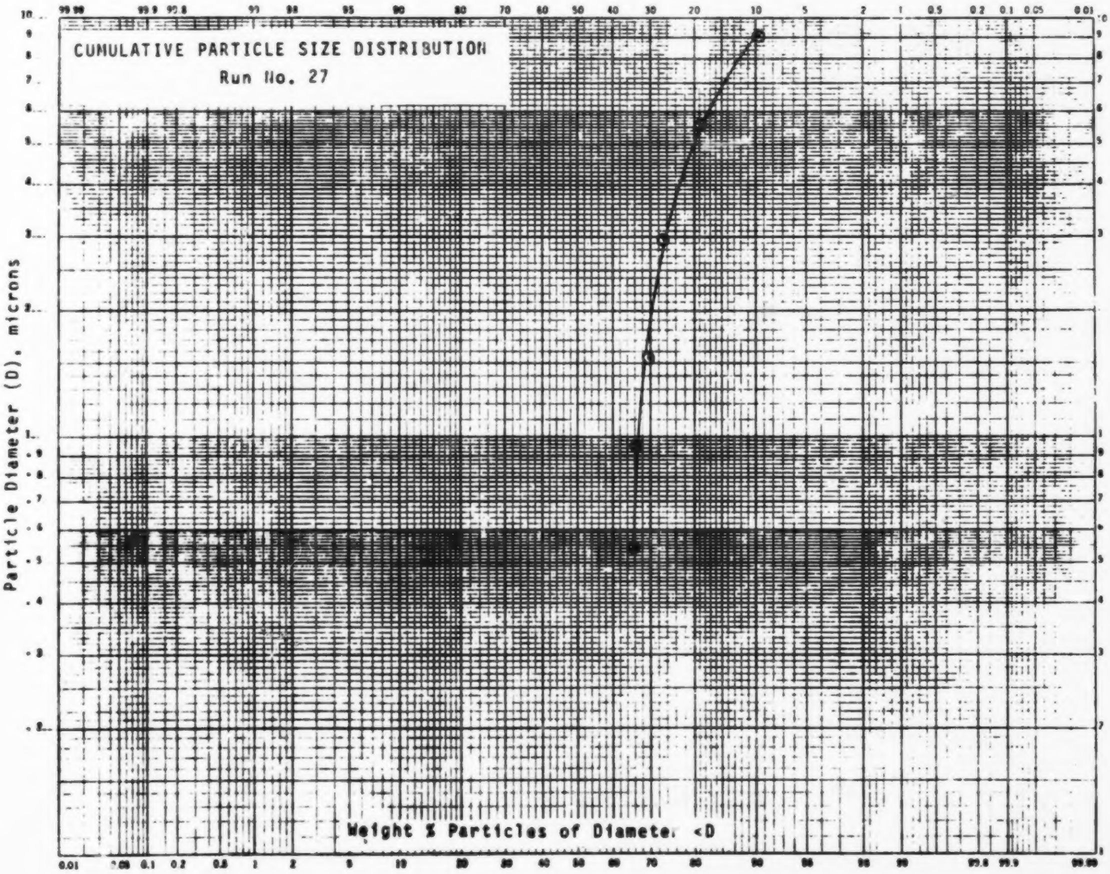
CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 21


CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 23
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99

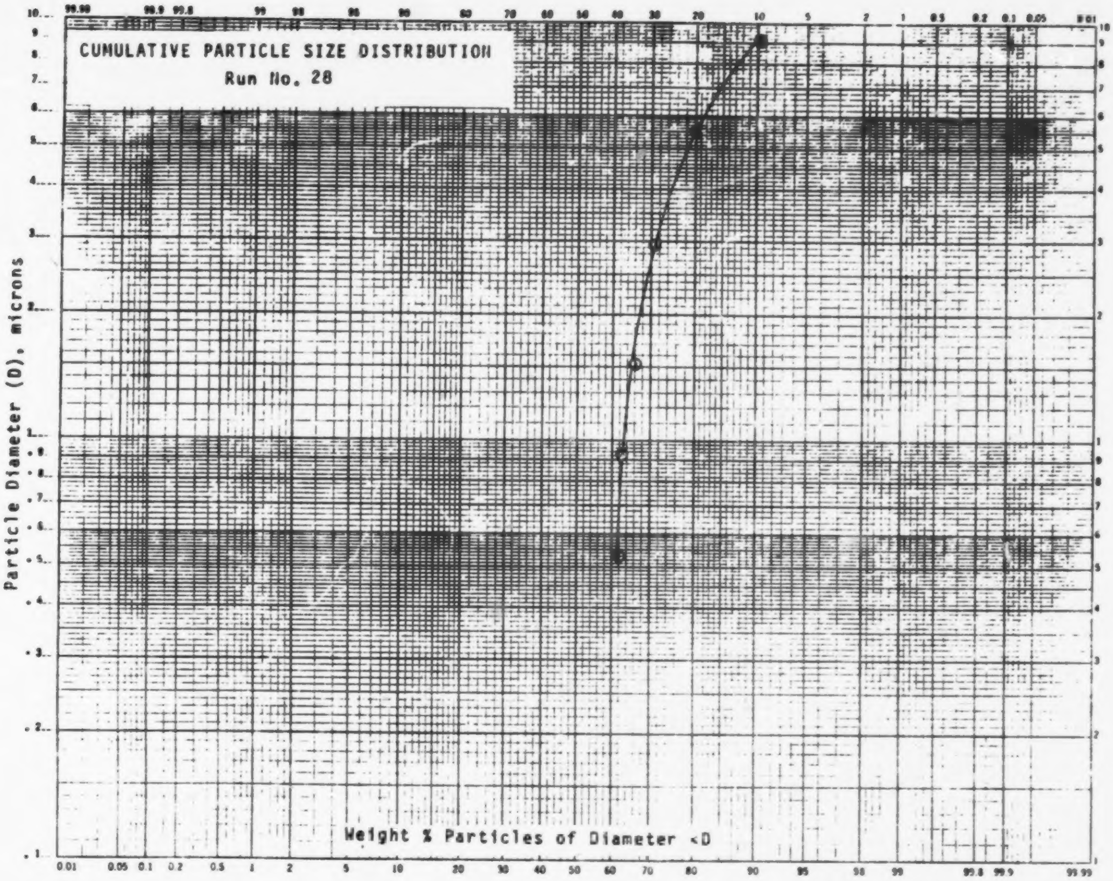

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 24
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99

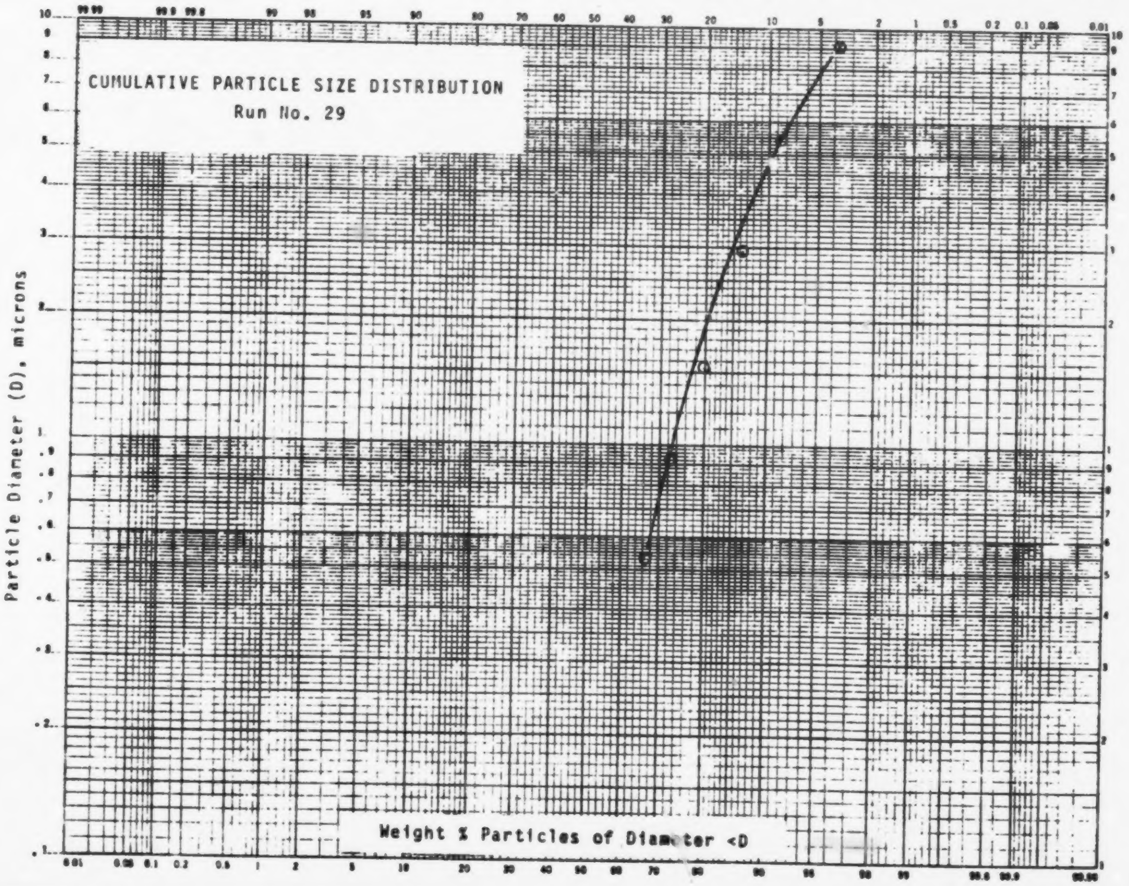


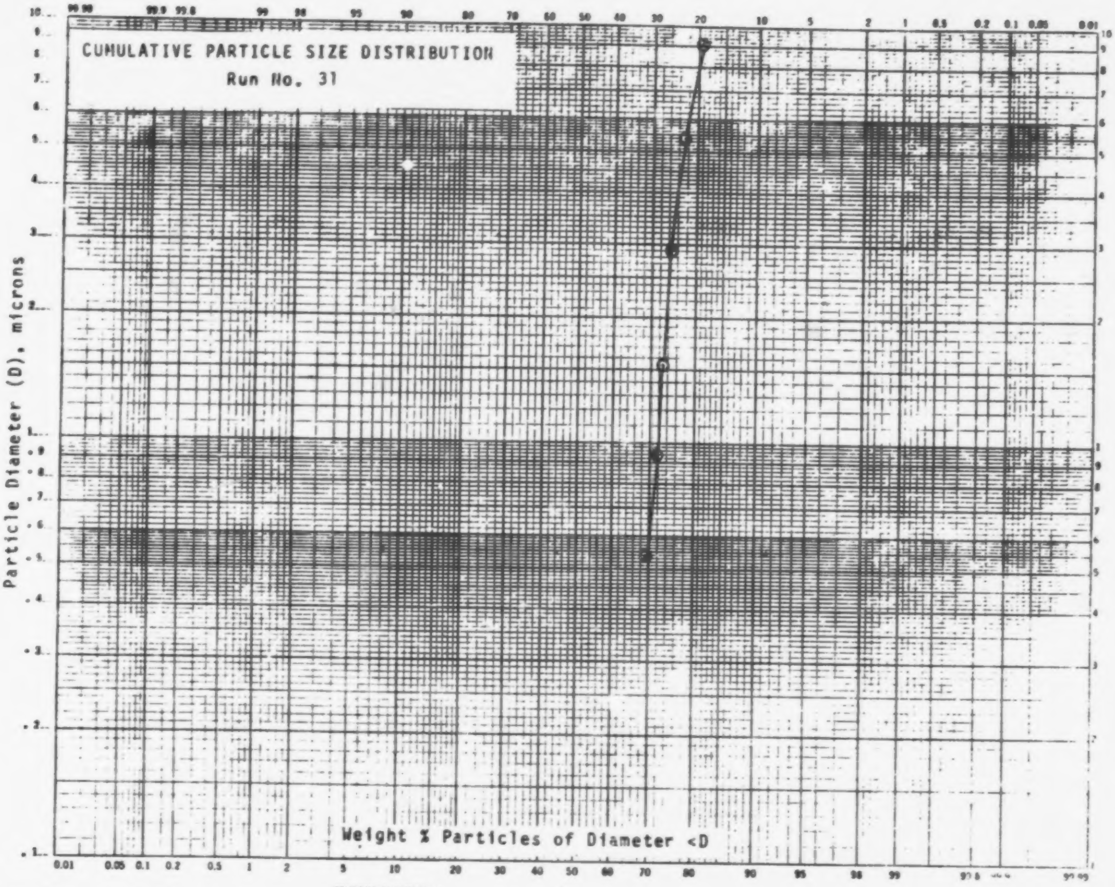
CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 25

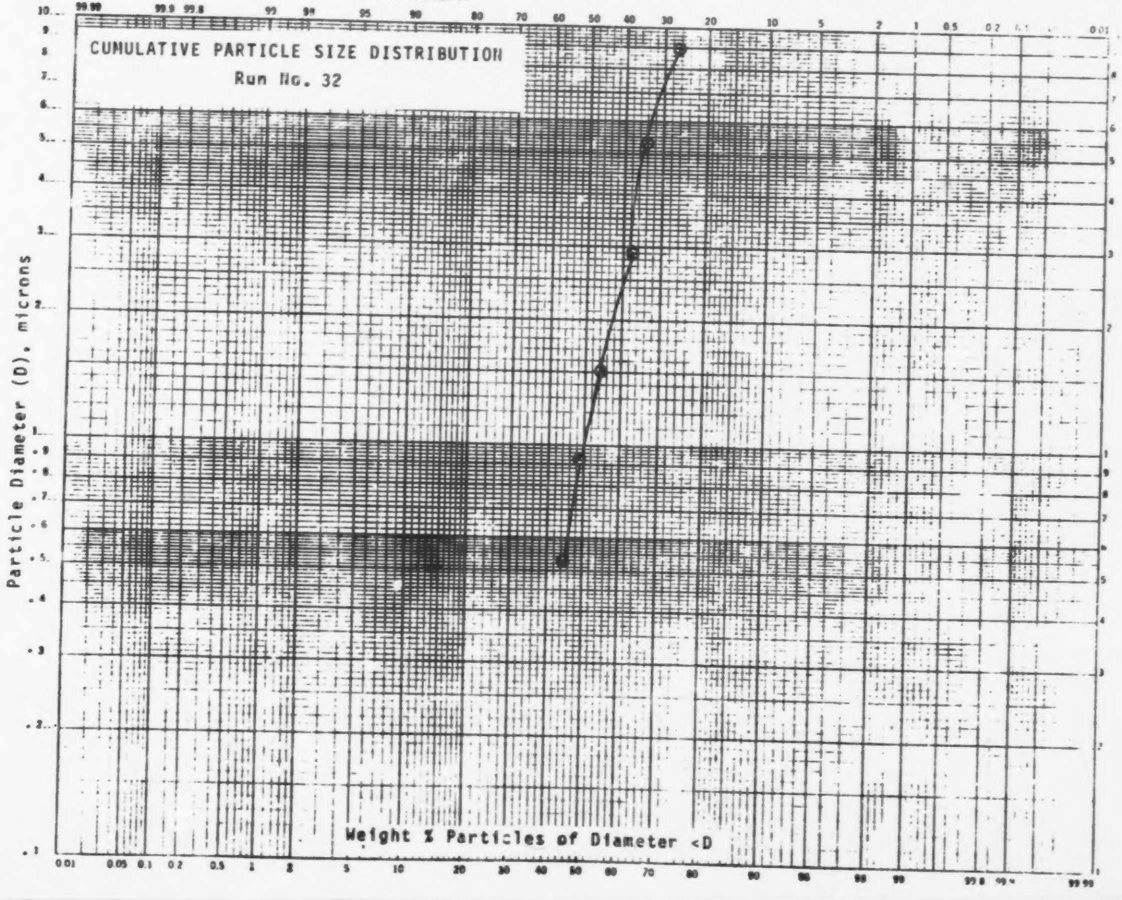


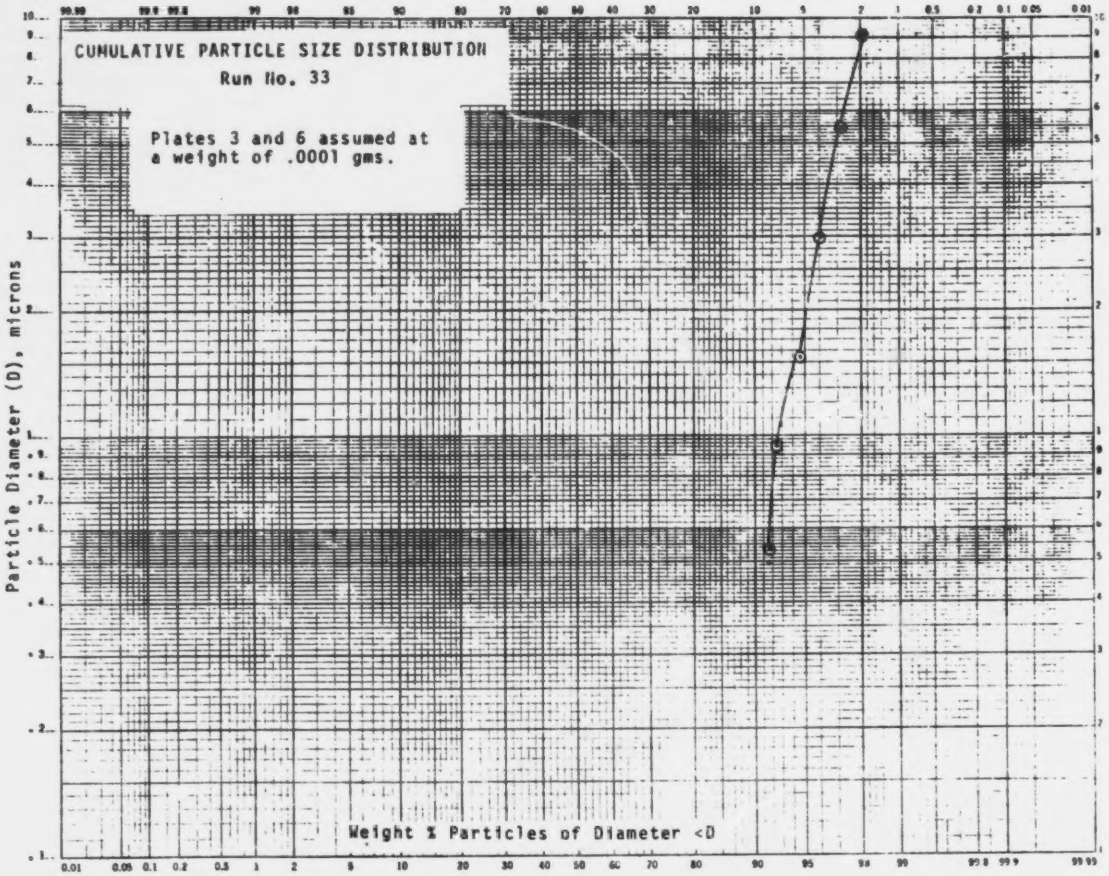
CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 27

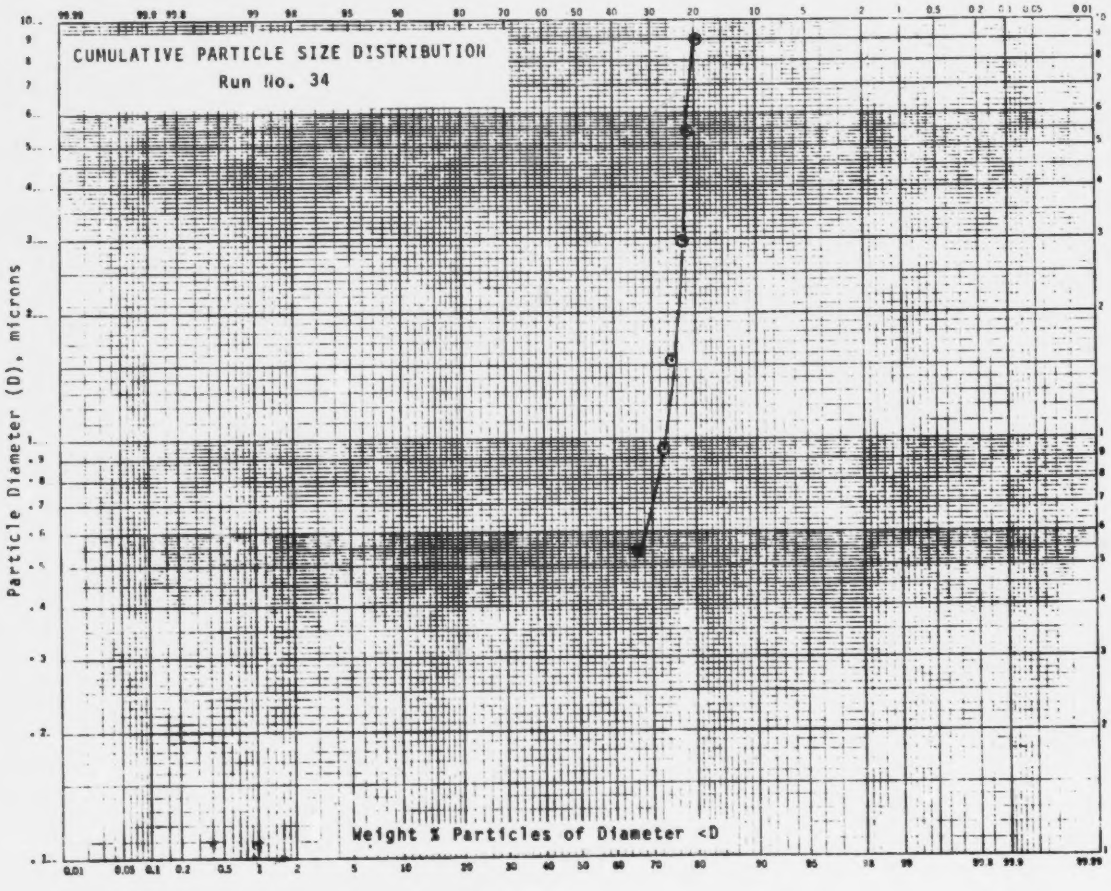

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 28
Particle Diameter (D), microns
Weight % Particles of Diameter <D

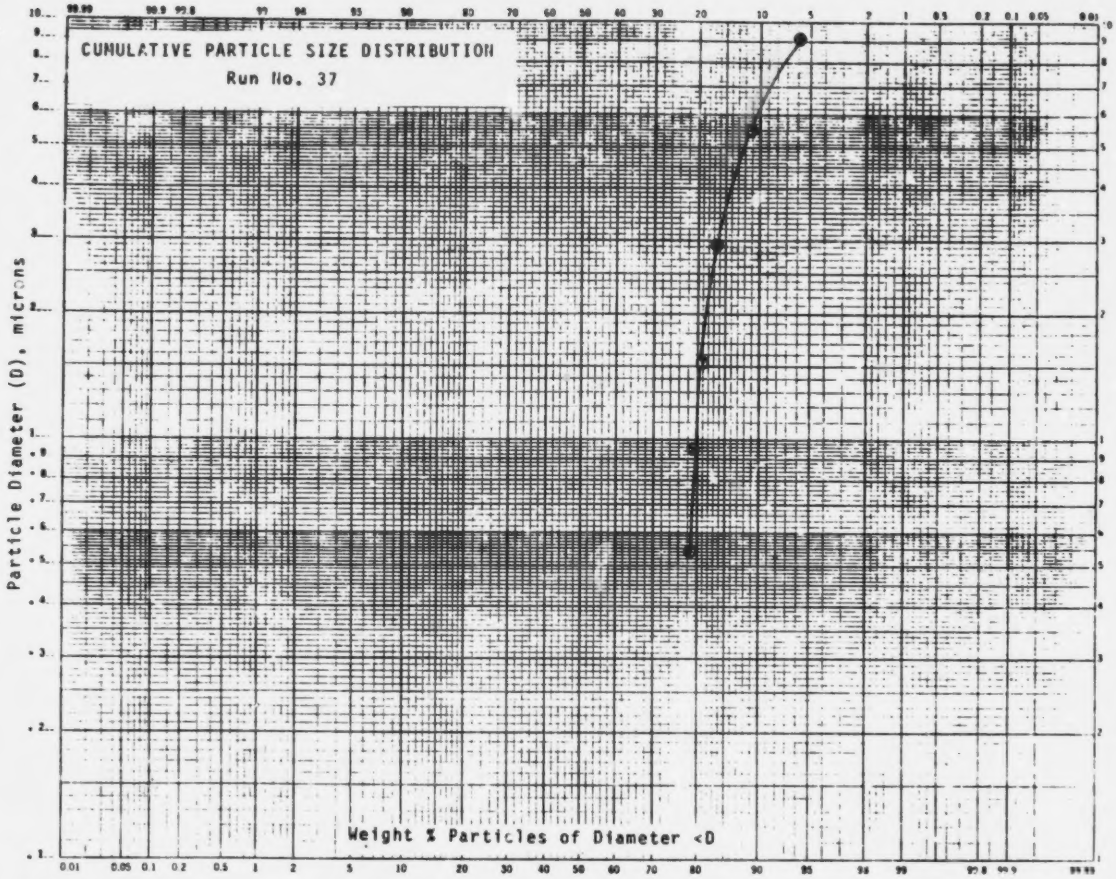

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 29
Particle Diameter (D), microns
Weight % Particles of Diameter <D


CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 31
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.99


CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 32
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.99

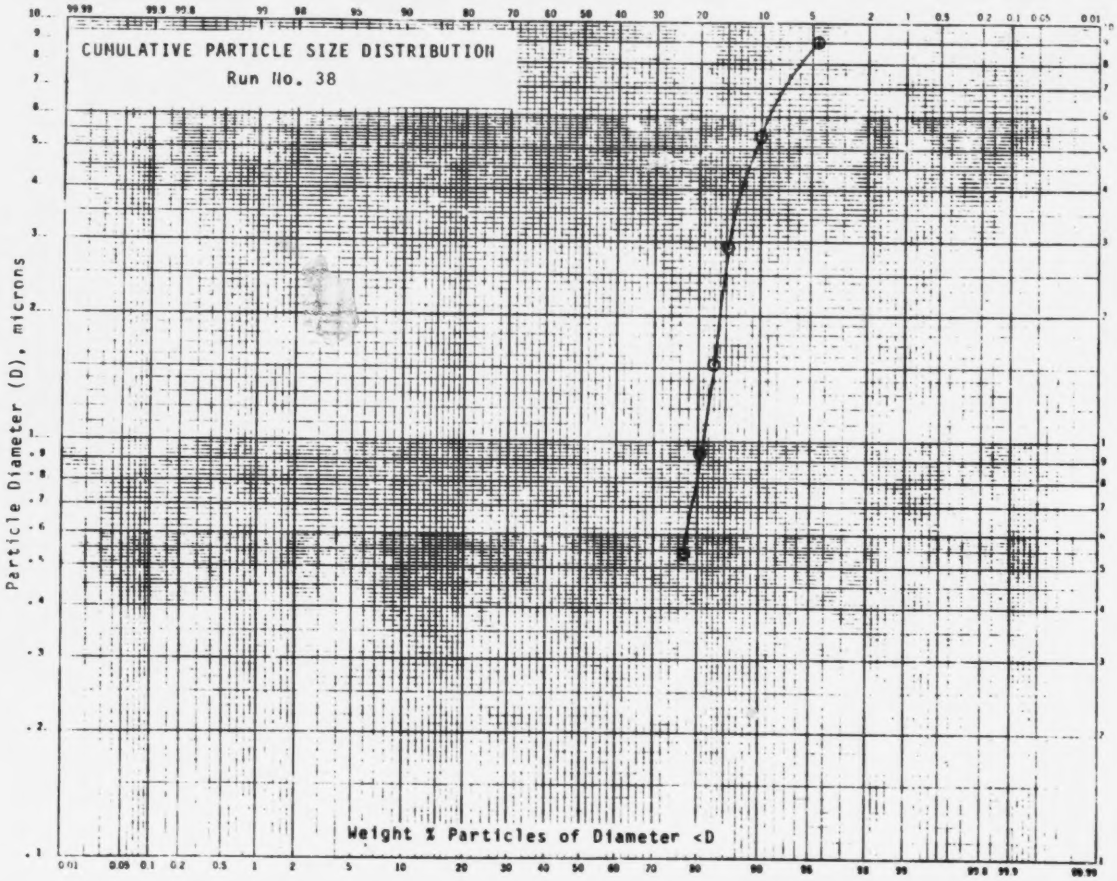

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 33
Plates 3 and 6 assumed at a weight of .0001 gms.
Particle Diameter (D), microns
Weight % Particles of Diameter <D


CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 34
Particle Diameter (D), microns
Weight % Particles of Diameter <D



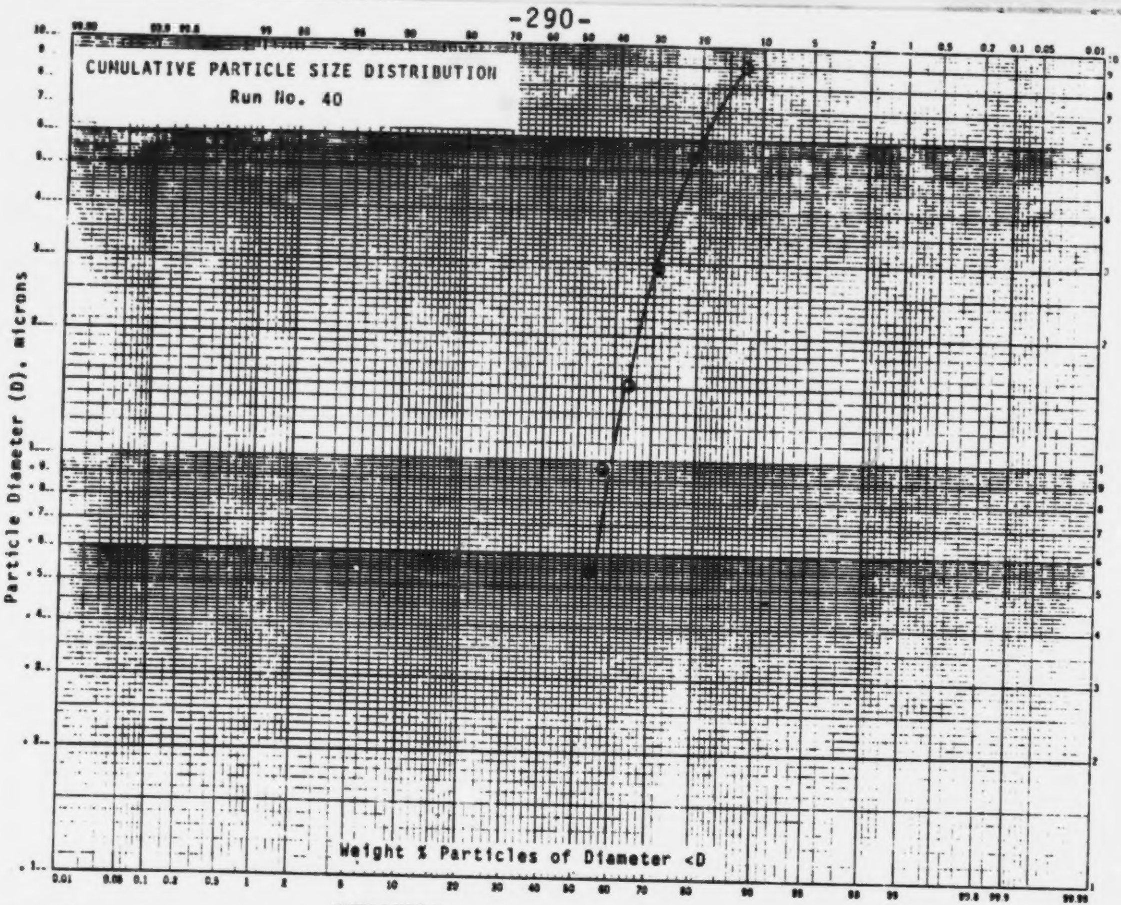
CUMULATIVE PARTICLE SIZE DISTRIBUTION

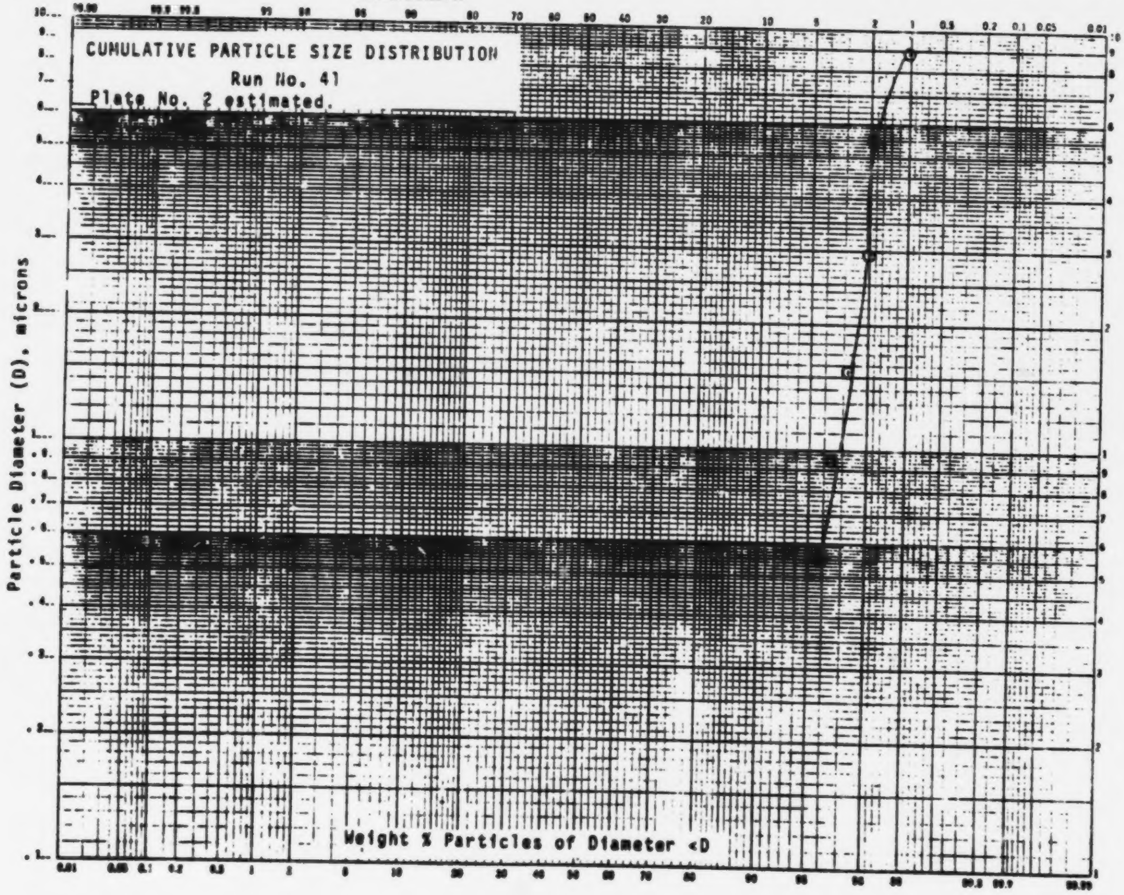
Run No. 37

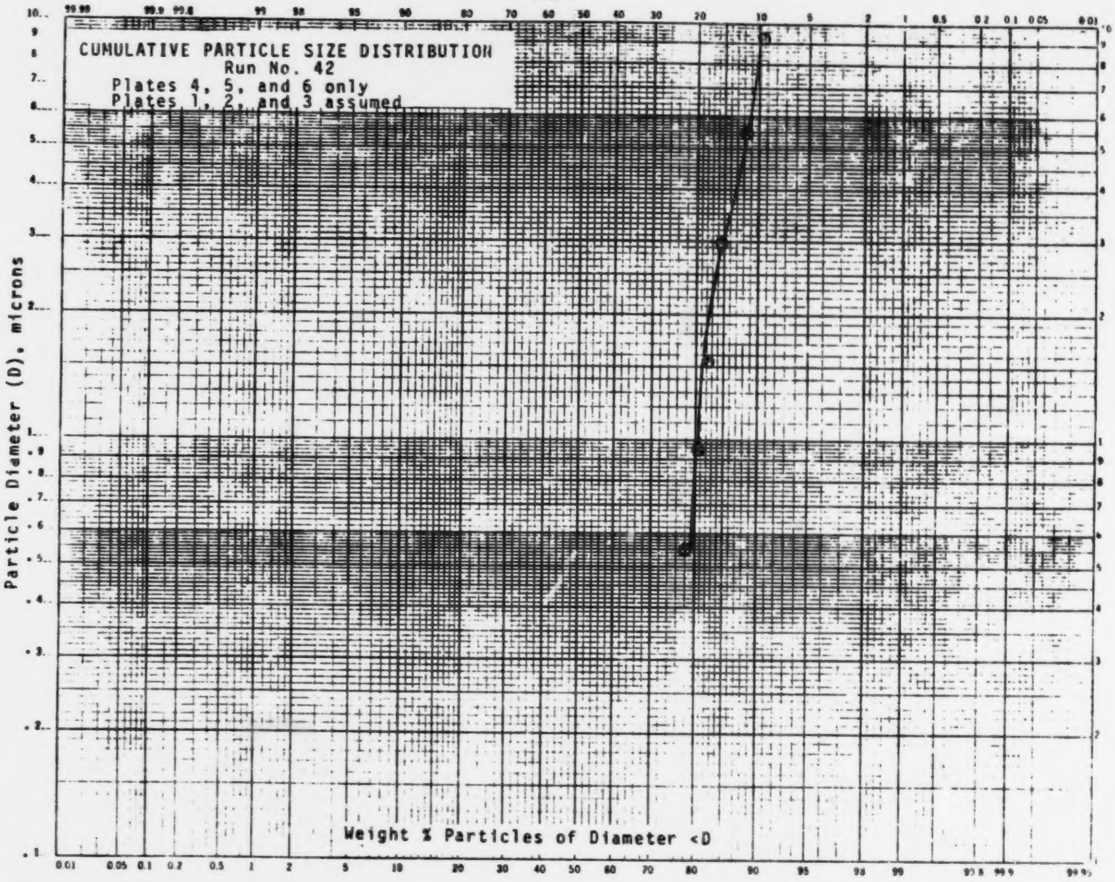


CUMULATIVE PARTICLE SIZE DISTRIBUTION

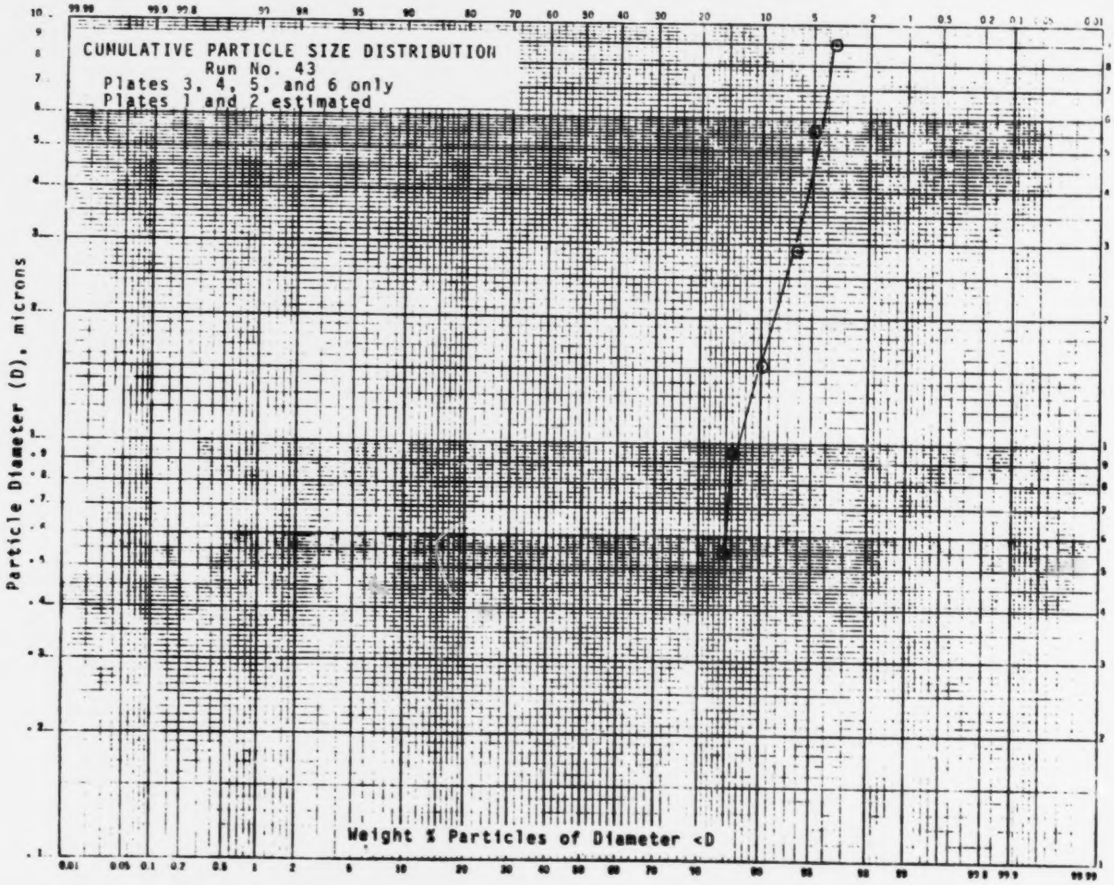
Run No. 38


CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 40

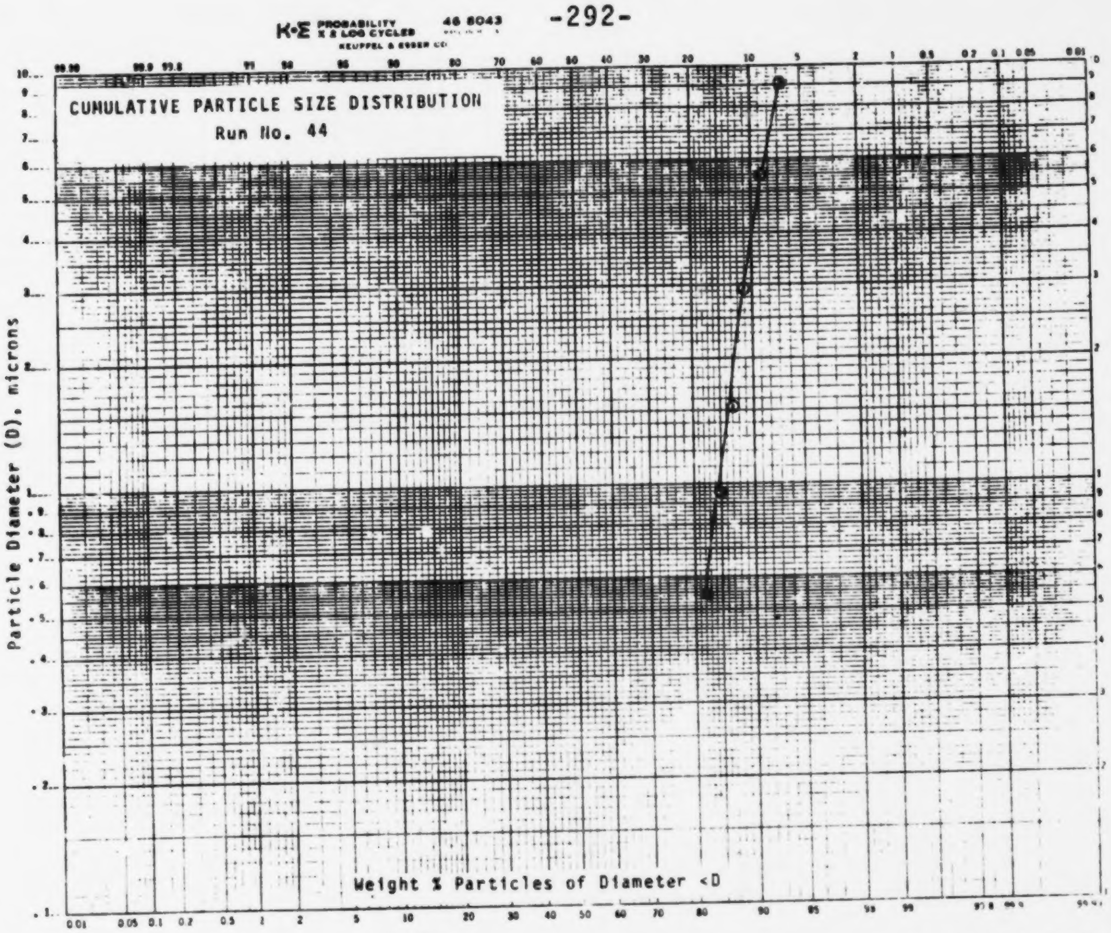

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 41
Plate No. 2 estimated.

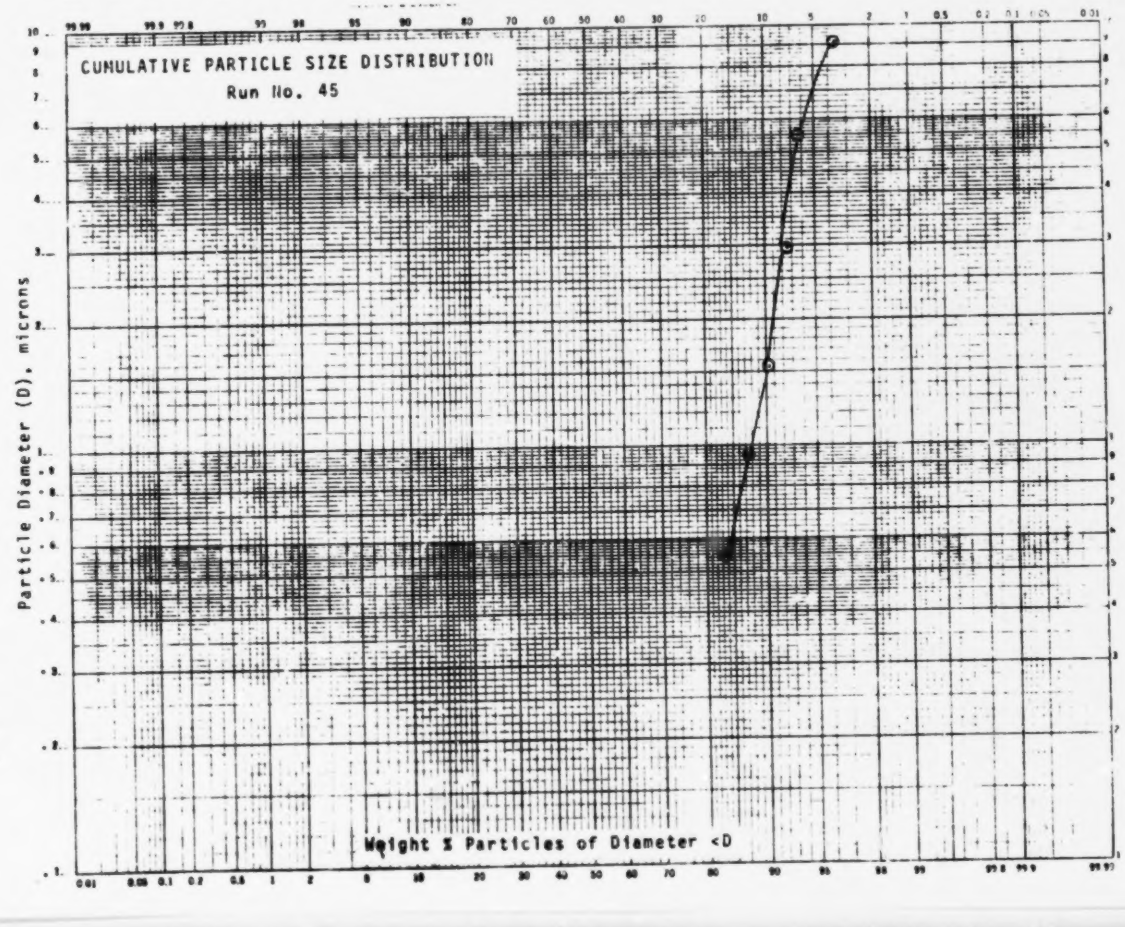


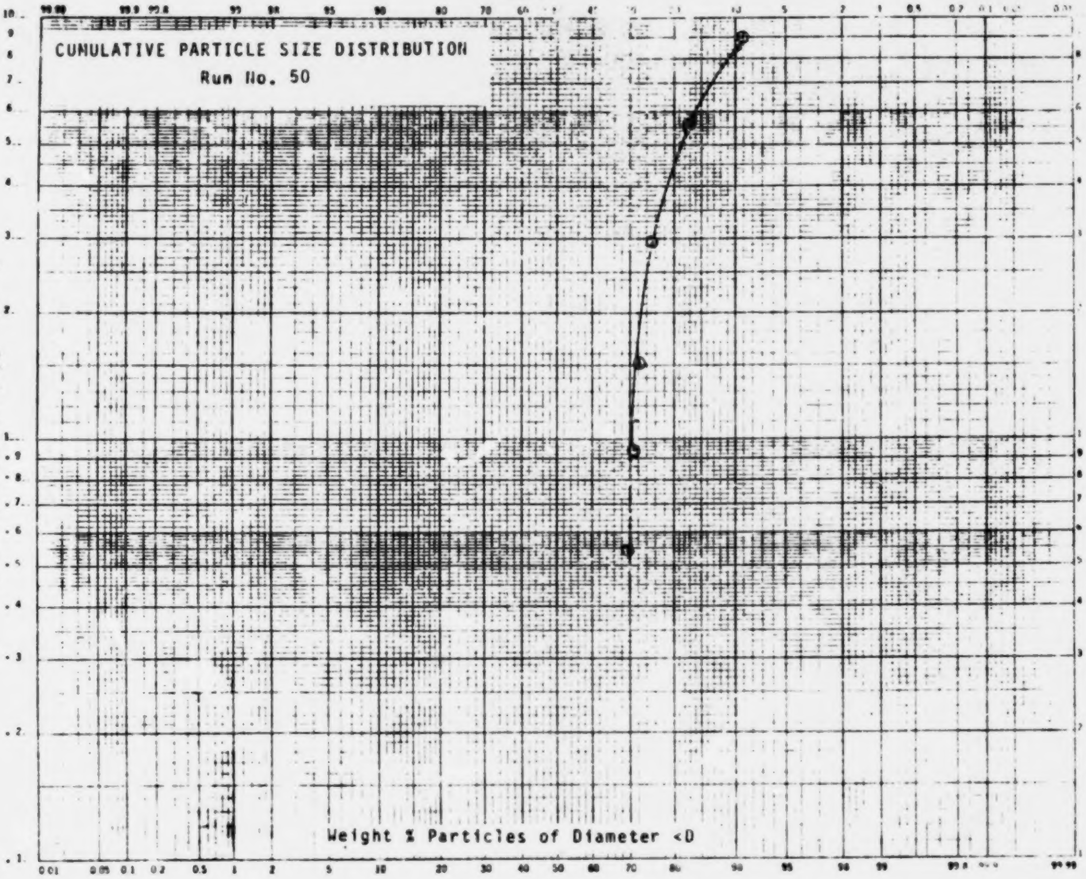
CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 42
Plates 4, 5, and 6 only
Plates 1, 2, and 3 assumed

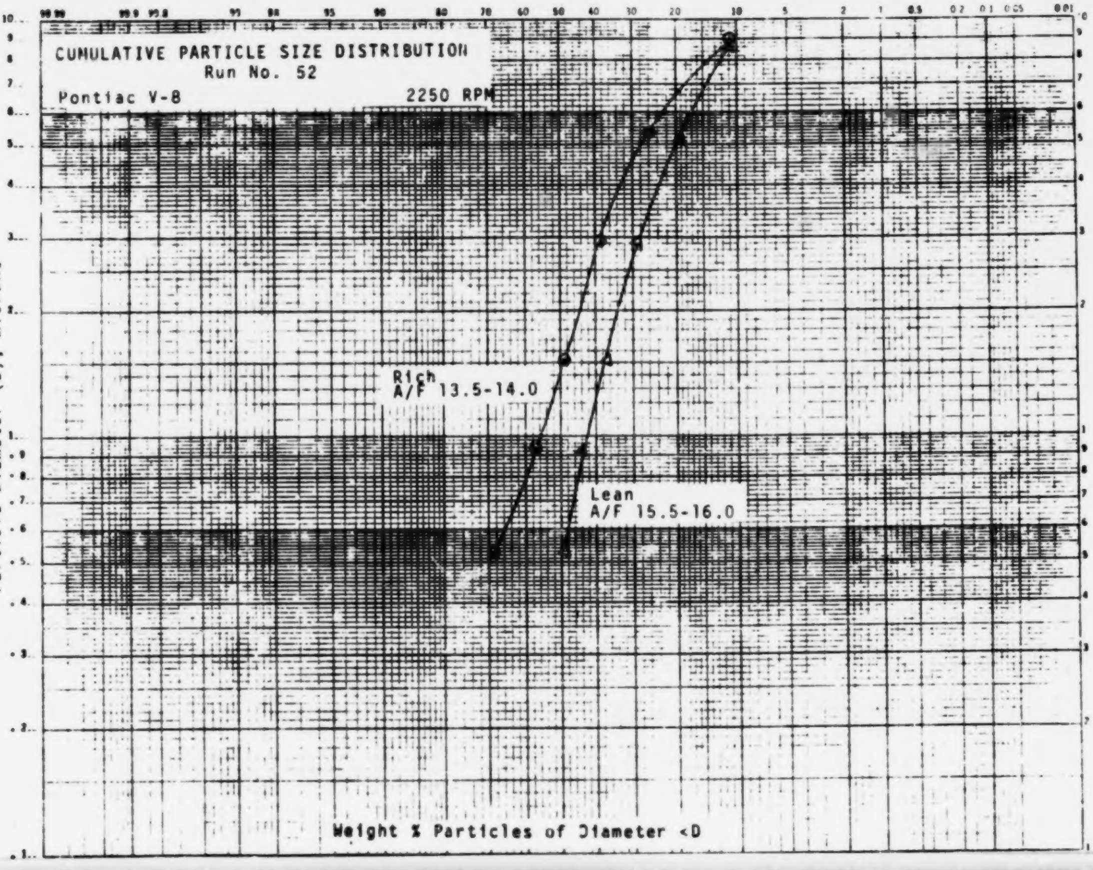


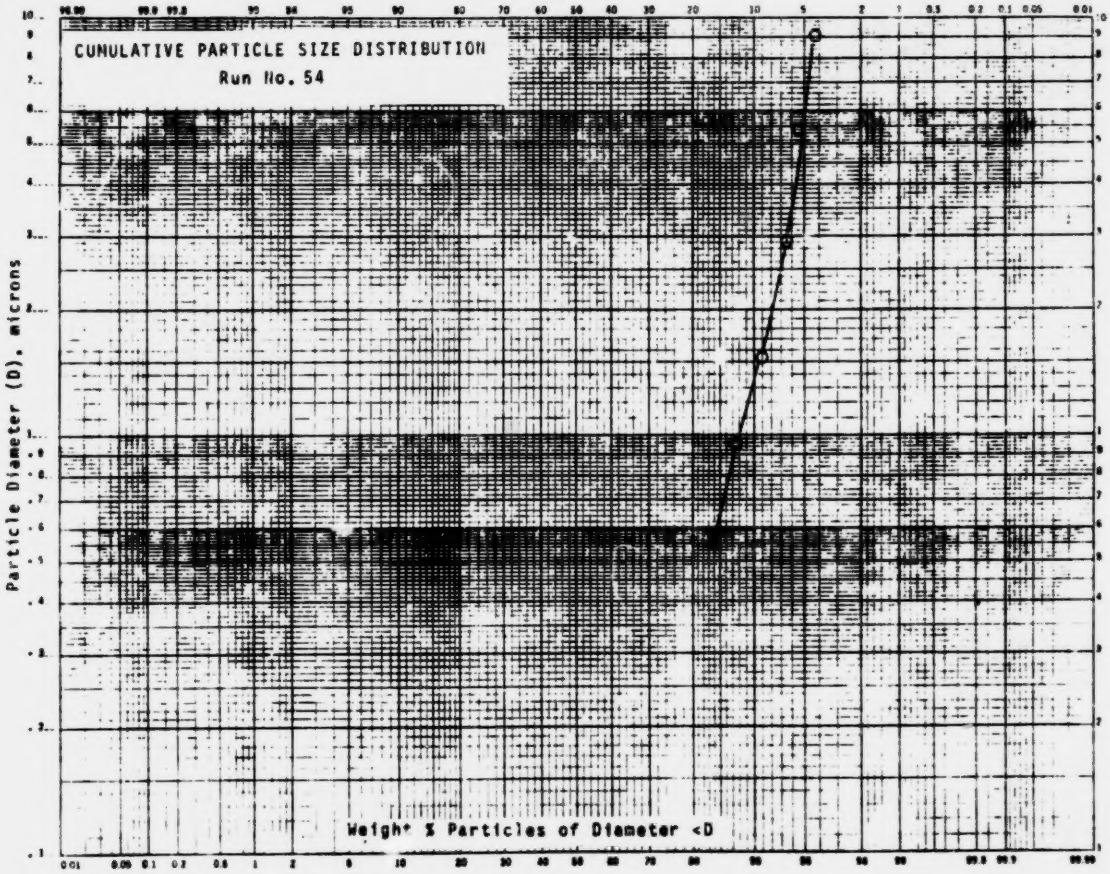
CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 43
Plates 3, 4, 5, and 6 only
Plates 1 and 2 estimated

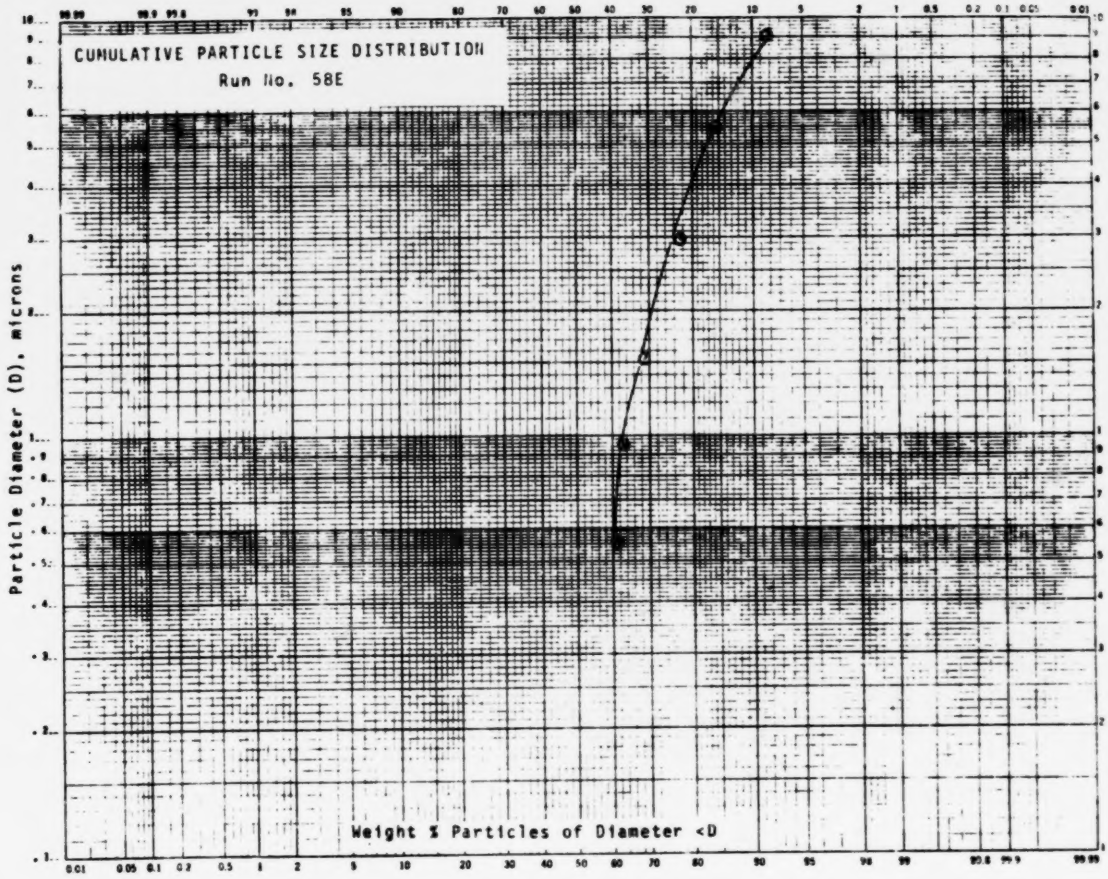

K•E PROBABILITY X 2 LOG CYCLES 46 8043
KEUFFEL & ESSER CO.
CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 44
Particle Diameter (D), microns
Weight % Particles of Diameter <D
99.99 99.9 99.8 99 98 95 90 80 70 60 50 40 30 20 10 5 2 1 0.5 0.2 0.1 0.05 0.01
0.01 0.05 0.1 0.2 0.5 1 2 5 10 20 30 40 50 60 70 80 90 95 98 99 99.8 99.9 99.99
10 9 8 7 6 5 4 3 2 1 .9 .8 .7 .6 .5 .4 .3 .2 .1

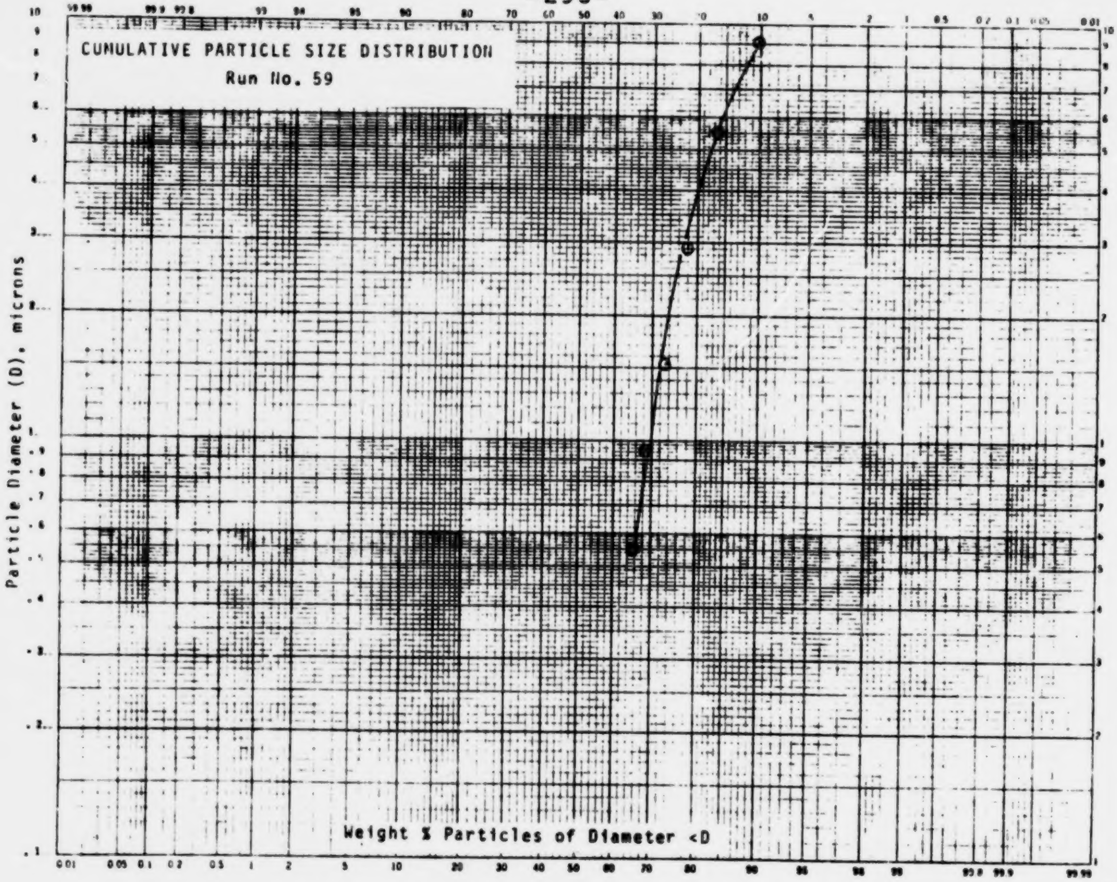

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 45
Particle Diameter (D), microns
Weight % Particles of Diameter <D
99.99 99.9 99.8 99 98 95 90 80 70 60 50 40 30 20 10 5 2 1 0.5 0.2 0.1 0.05 0.01
0.01 0.05 0.1 0.2 0.5 1 2 5 10 20 30 40 50 60 70 80 90 95 98 99 99.8 99.9 99.99
10 9 8 7 6 5 4 3 2 1 .9 .8 .7 .6 .5 .4 .3 .2 .1

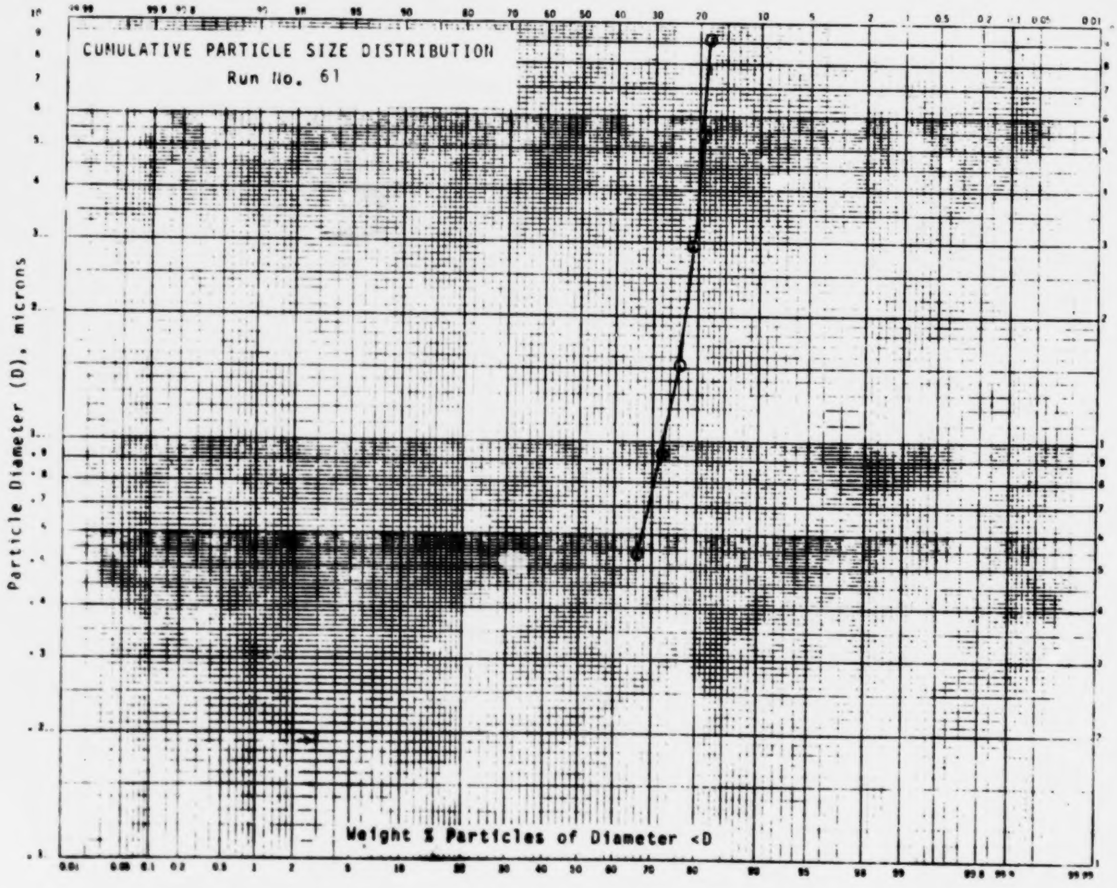

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 50
Particle Diameter (D), microns
Weight % Particles of Diameter <D
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.99

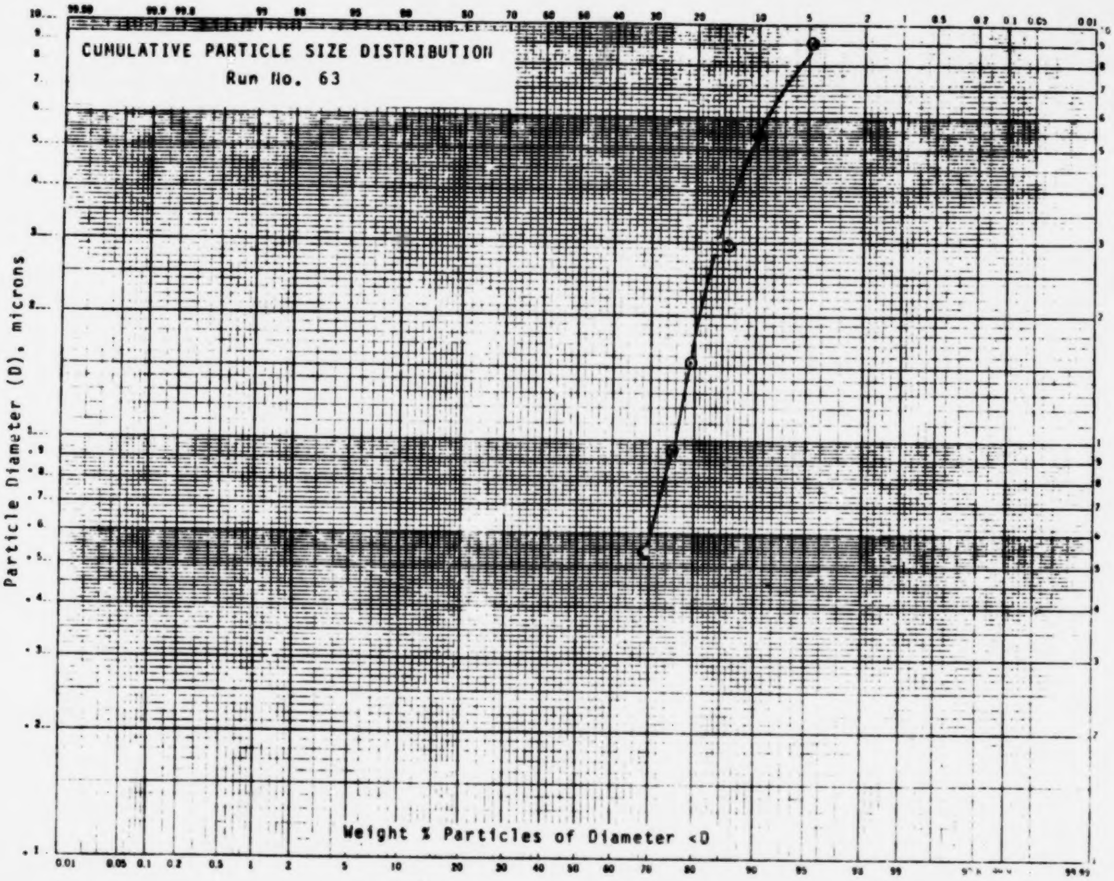

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 52
Pontiac V-8
2250 RPM
Rich
A/F 13.5-14.0
Lean
A/F 15.5-16.0
Particle Diameter (D), microns
Weight % Particles of Diameter <D
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1
99.99
99.9
99.8
99
98
95
90
80
70
60
50
40
30
20
10
5
2
1
0.5
0.2
0.1
0.05
0.01

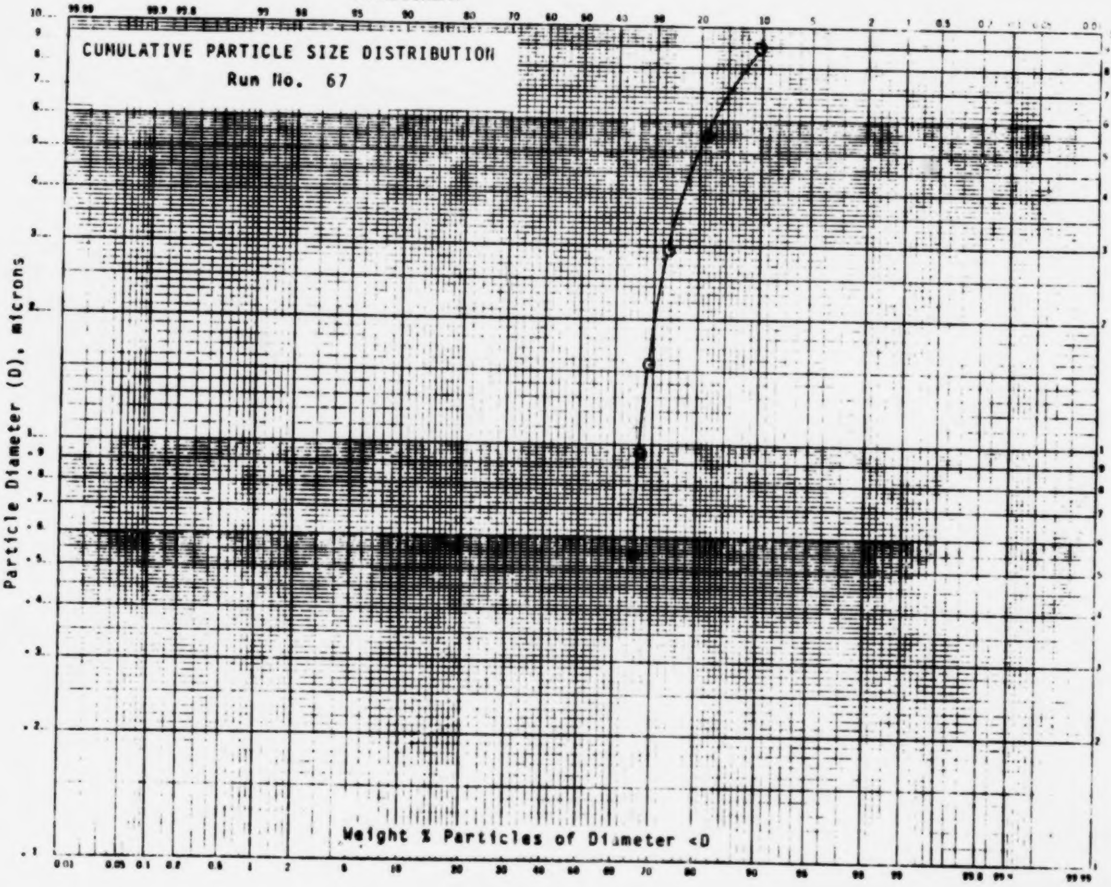

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 54
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99

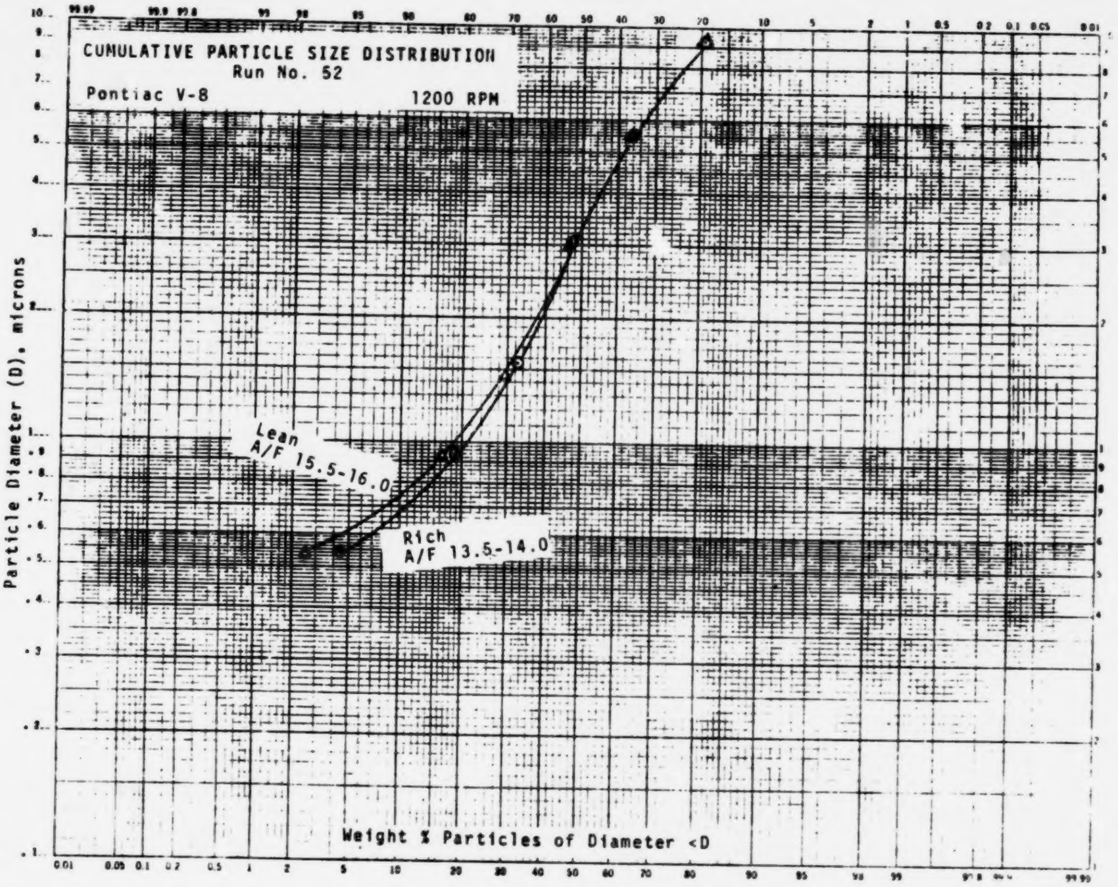

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 58E
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99

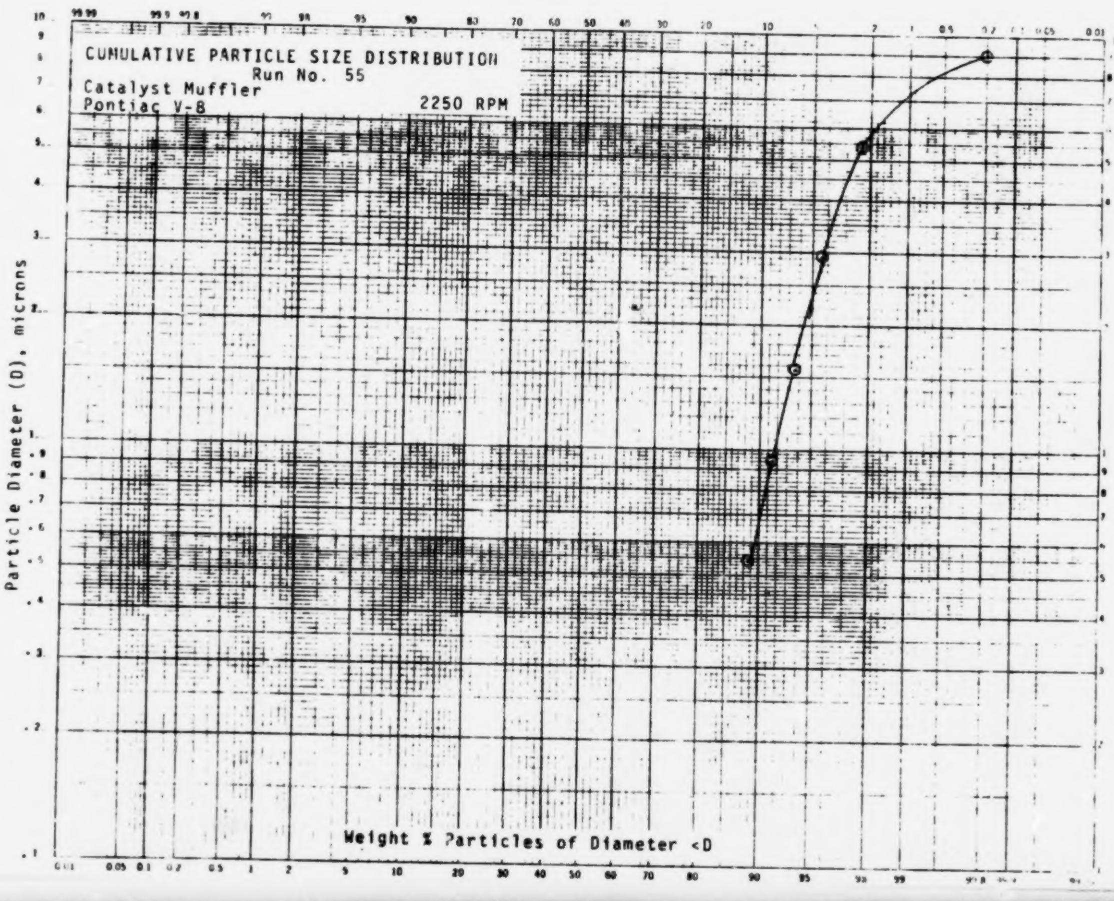

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 59
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99

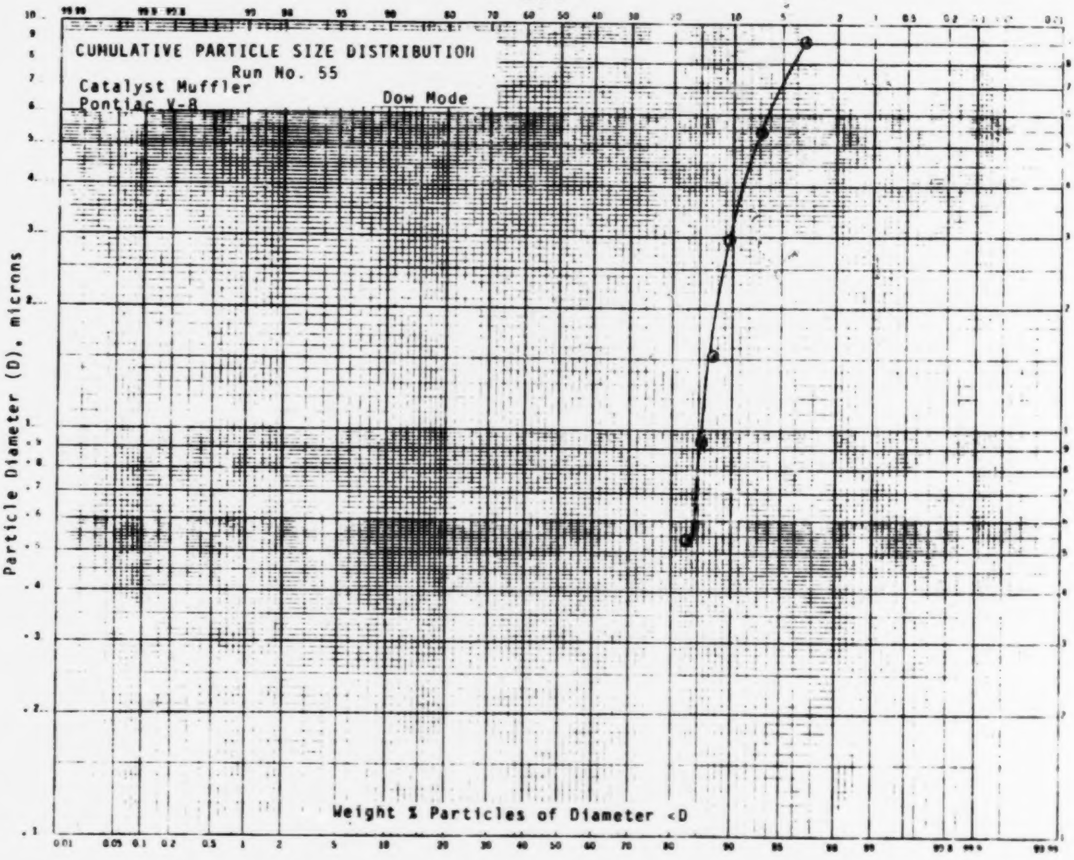

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 61
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99

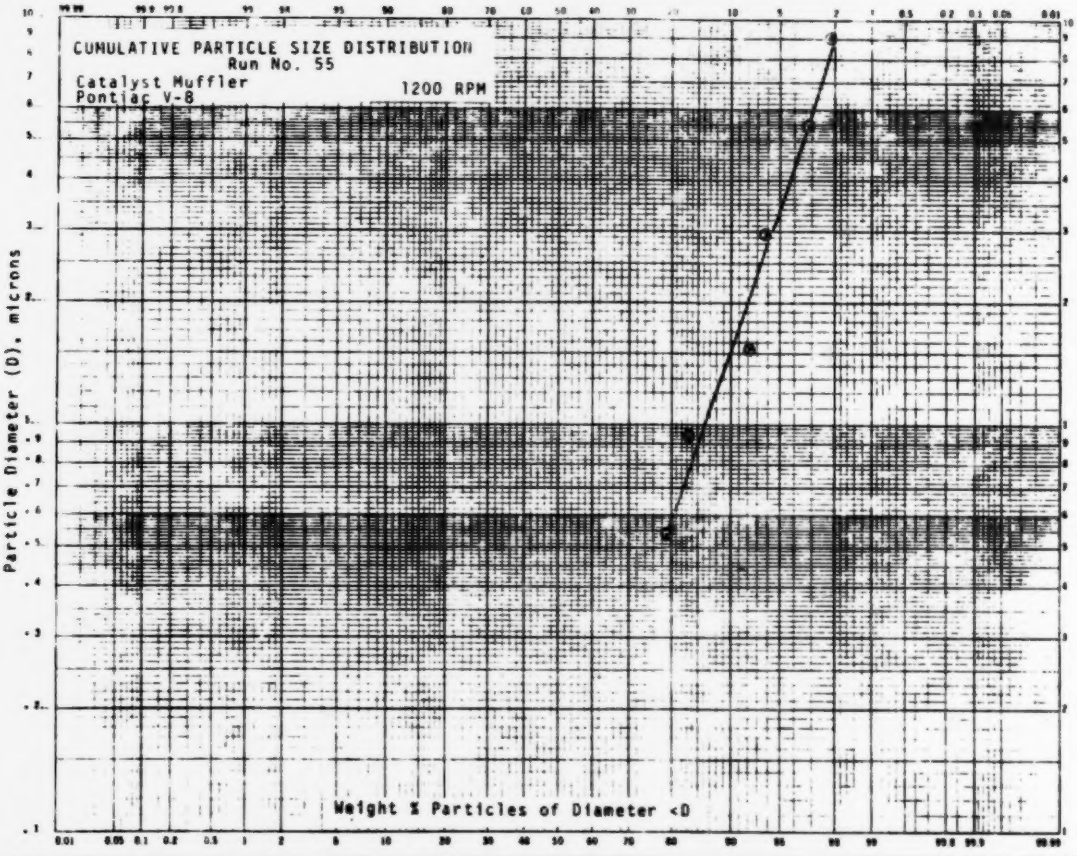

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 63
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.99

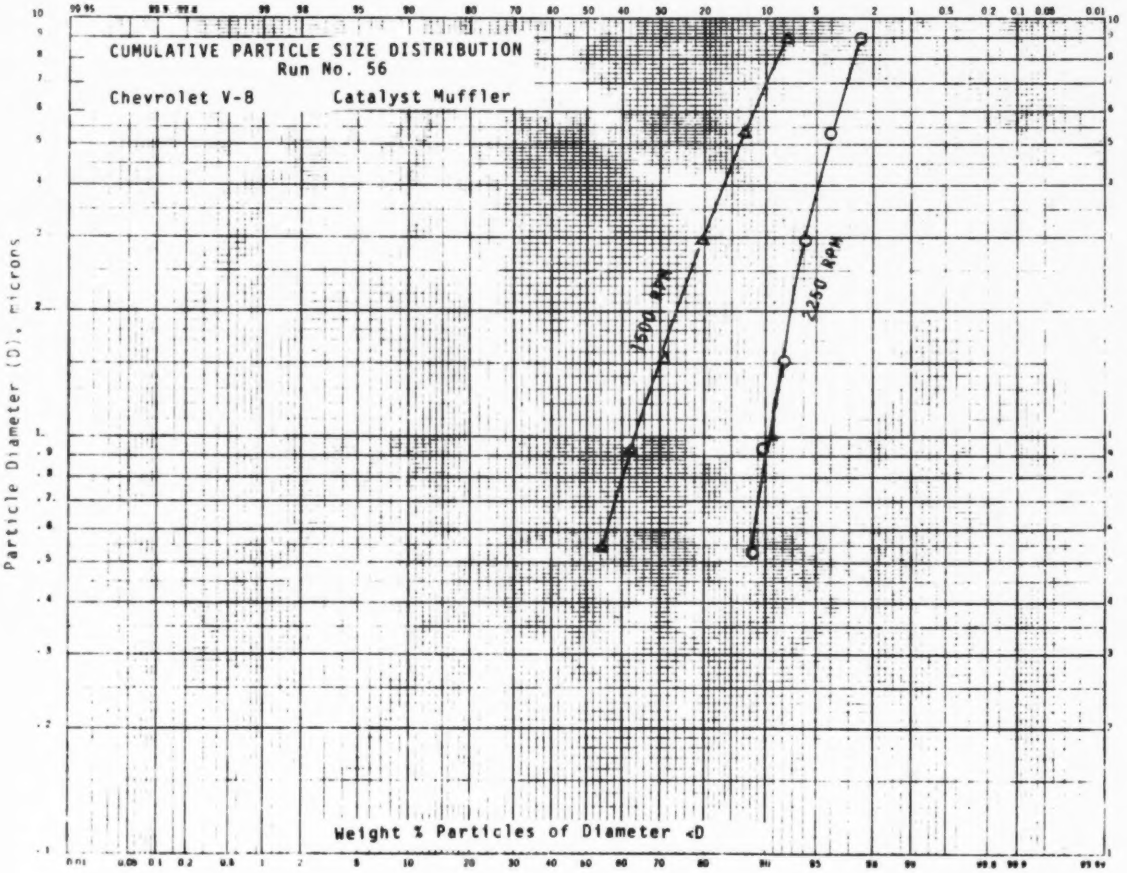

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 67
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.99


CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 52
Pontiac V-8
1200 RPM
Lean
A/F 15.5-16.0
Rich
A/F 13.5-14.0
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.99


CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 55
Catalyst Muffler
Pontiac V-8
2250 RPM
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99


CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 55
Catalyst Muffler
Pontiac V-8
Dow Mode
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99


CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 55
Catalyst Muffler
Pontiac V-8
1200 RPM
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99

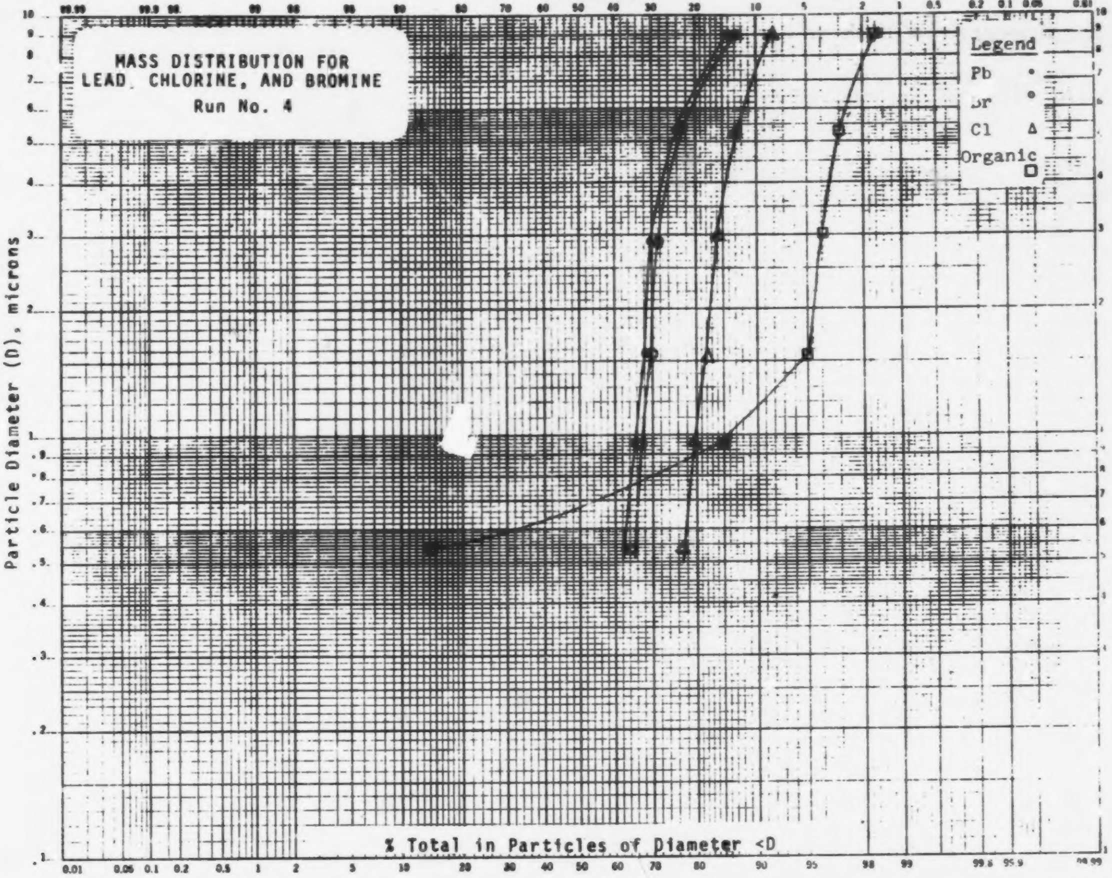


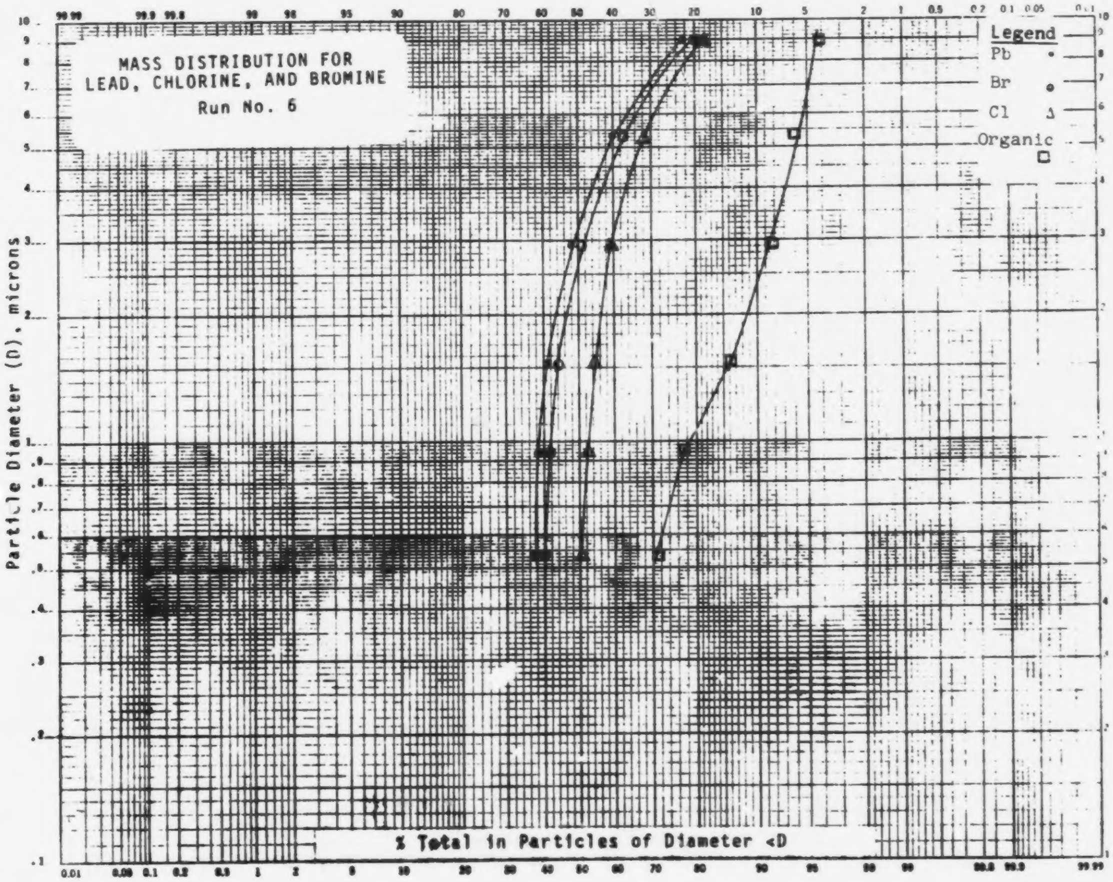
CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 56

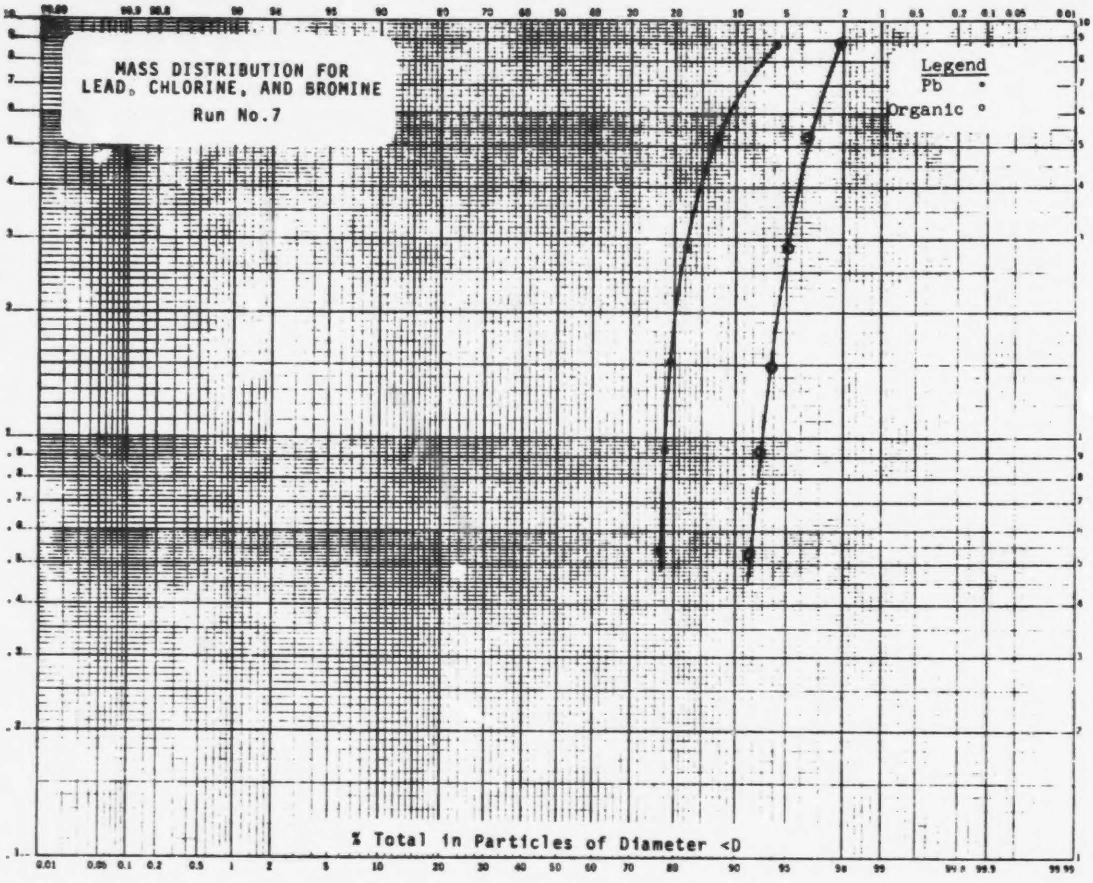
Chevrolet V-8 Catalyst Muffler

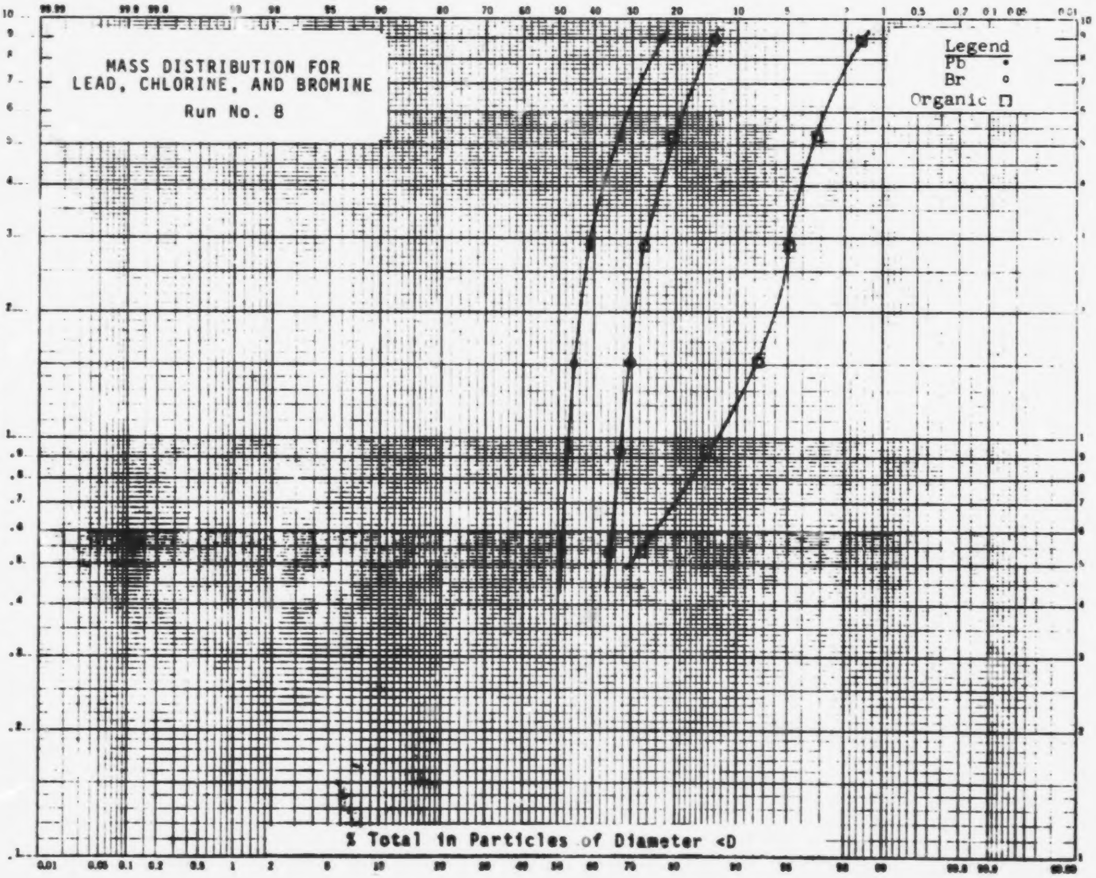
APPENDIX C

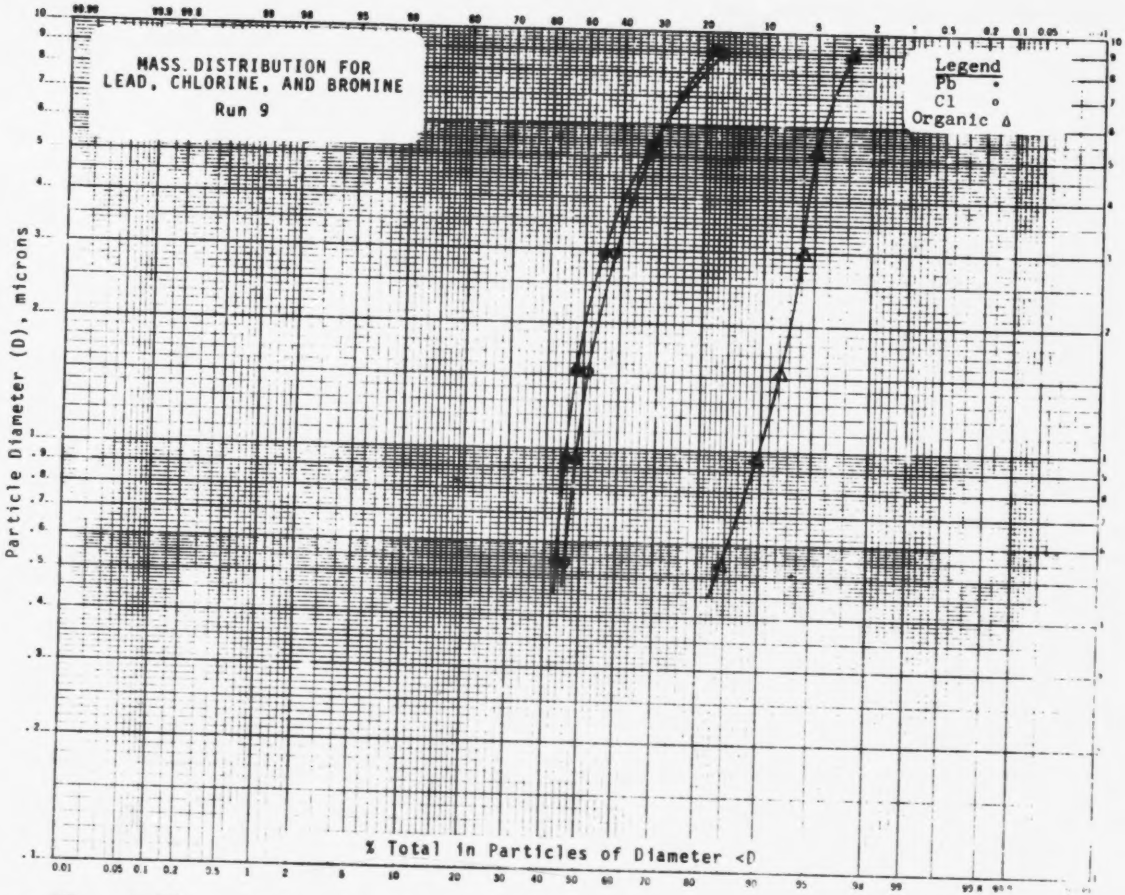
Mass Distribution for Lead, Chlorine, Bromine, and Organics

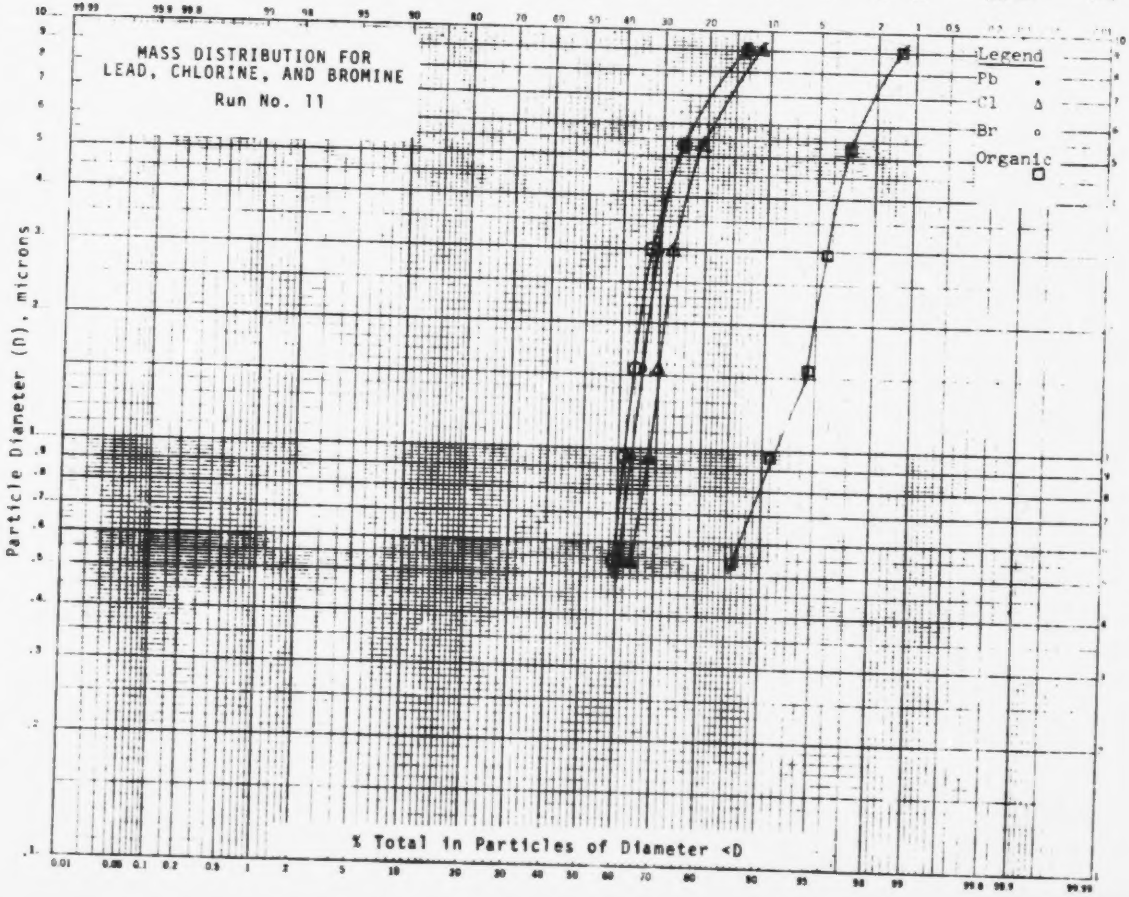

MASS DISTRIBUTION FOR
LEAD, CHLORINE, AND BROMINE
Run No. 4
Legend
Pb •
Br ○
Cl Δ
Organic □
Particle Diameter (D), microns
% Total in Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.99

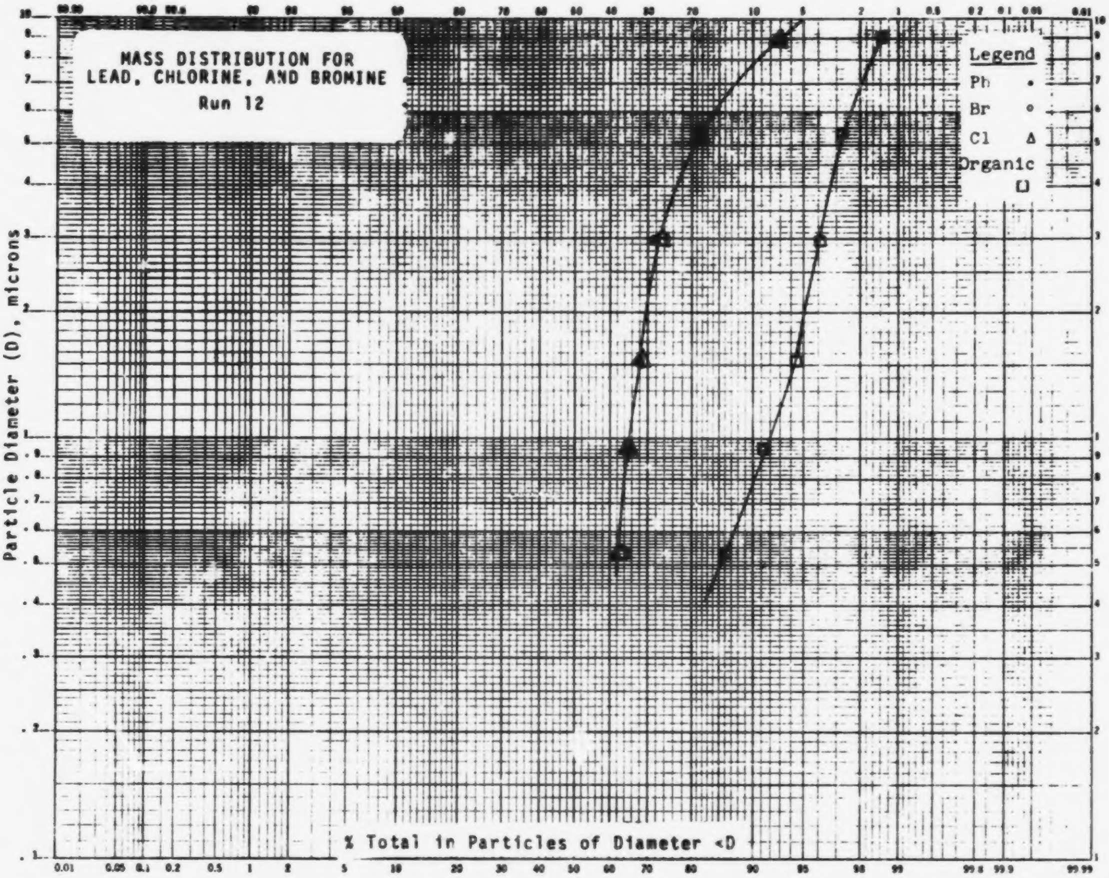

MASS DISTRIBUTION FOR
LEAD, CHLORINE, AND BROMINE
Run No. 6
Legend
Pb •
Br ○
Cl Δ
Organic □
Particle Diameter (D), microns
% Total in Particles of Diameter <D
0.01
0.1
0.2
1
2
10
20
30
40
50
60
70
80
90
95
98
99
99.99

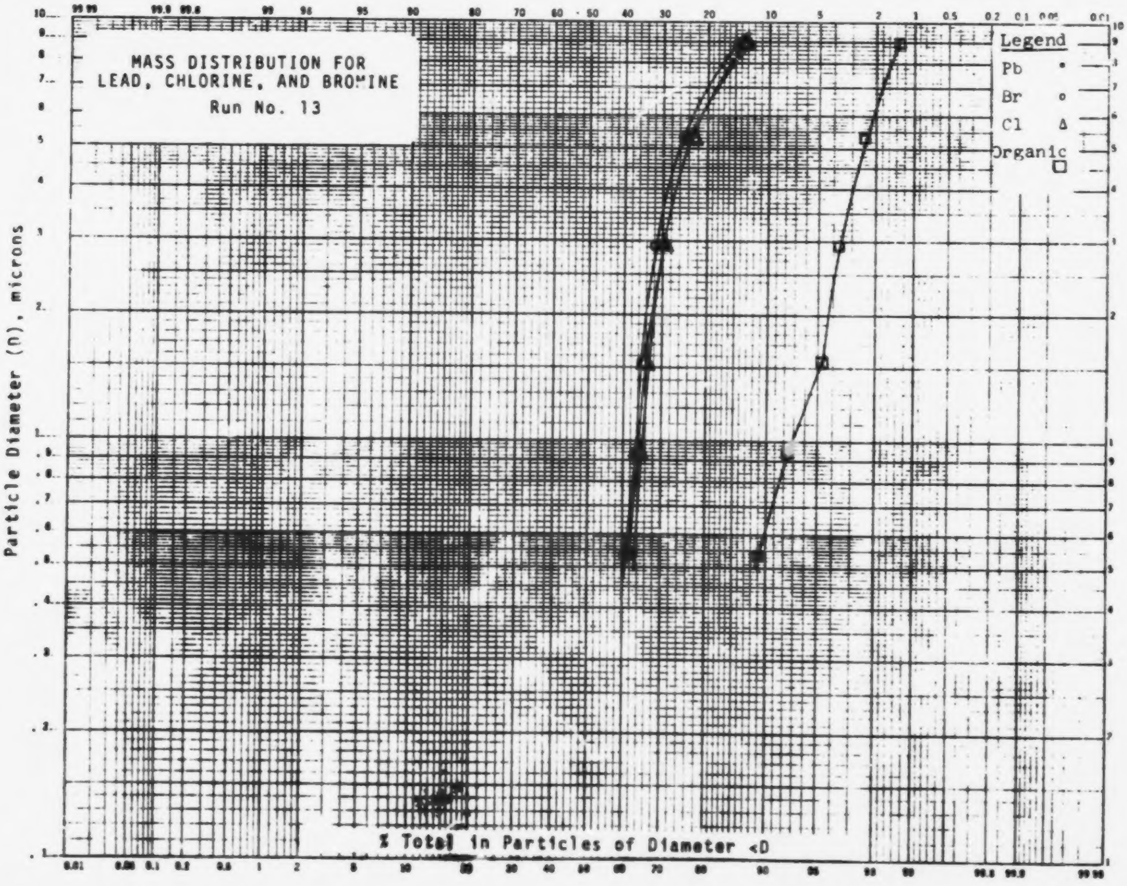

MASS DISTRIBUTION FOR
LEAD, CHLORINE, AND BROMINE
Run No.7
Legend
Pb •
Organic ○
Particle Diameter (D), microns
% Total in Particles of Diameter <D

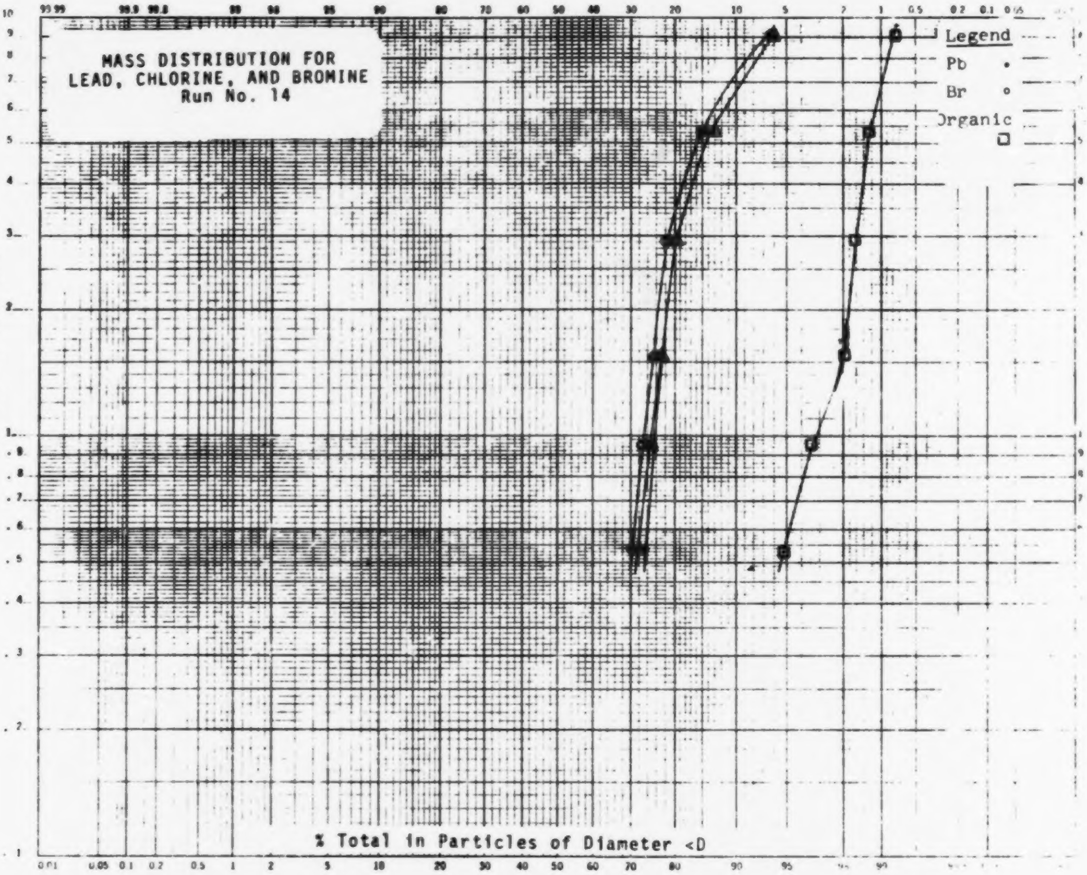

MASS DISTRIBUTION FOR
LEAD, CHLORINE, AND BROMINE
Run No. 8
Legend
Pb •
Br ○
Organic □
Particle Diameter (D), microns
% Total in Particles of Diameter <D

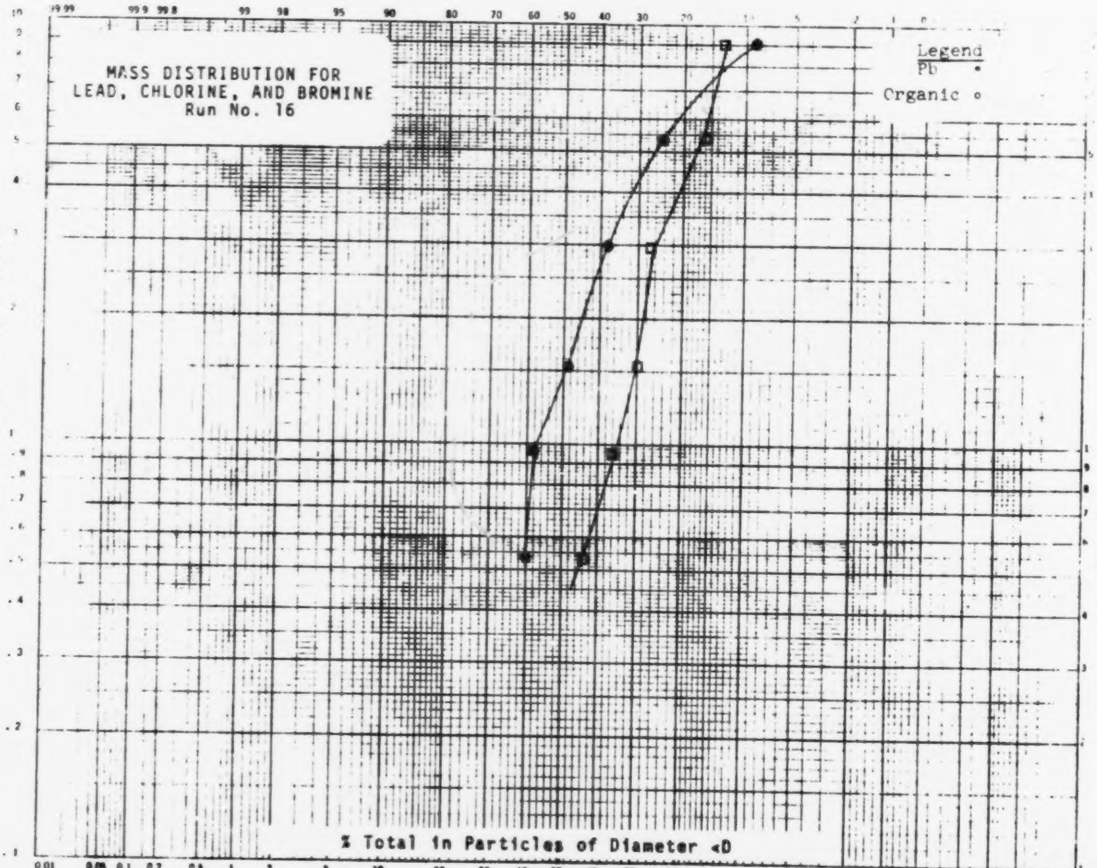

MASS. DISTRIBUTION FOR LEAD, CHLORINE, AND BROMINE
Run 9

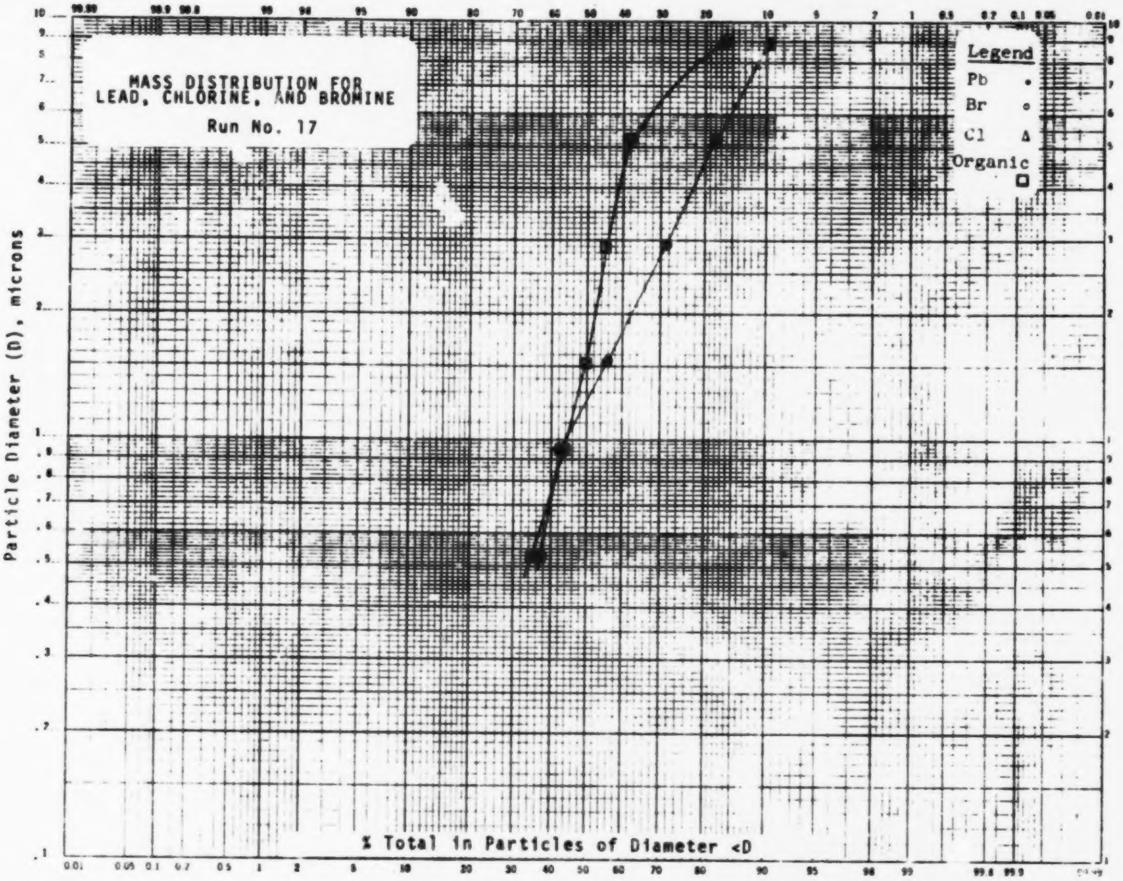

MASS DISTRIBUTION FOR LEAD, CHLORINE, AND BROMINE
Run No. 11

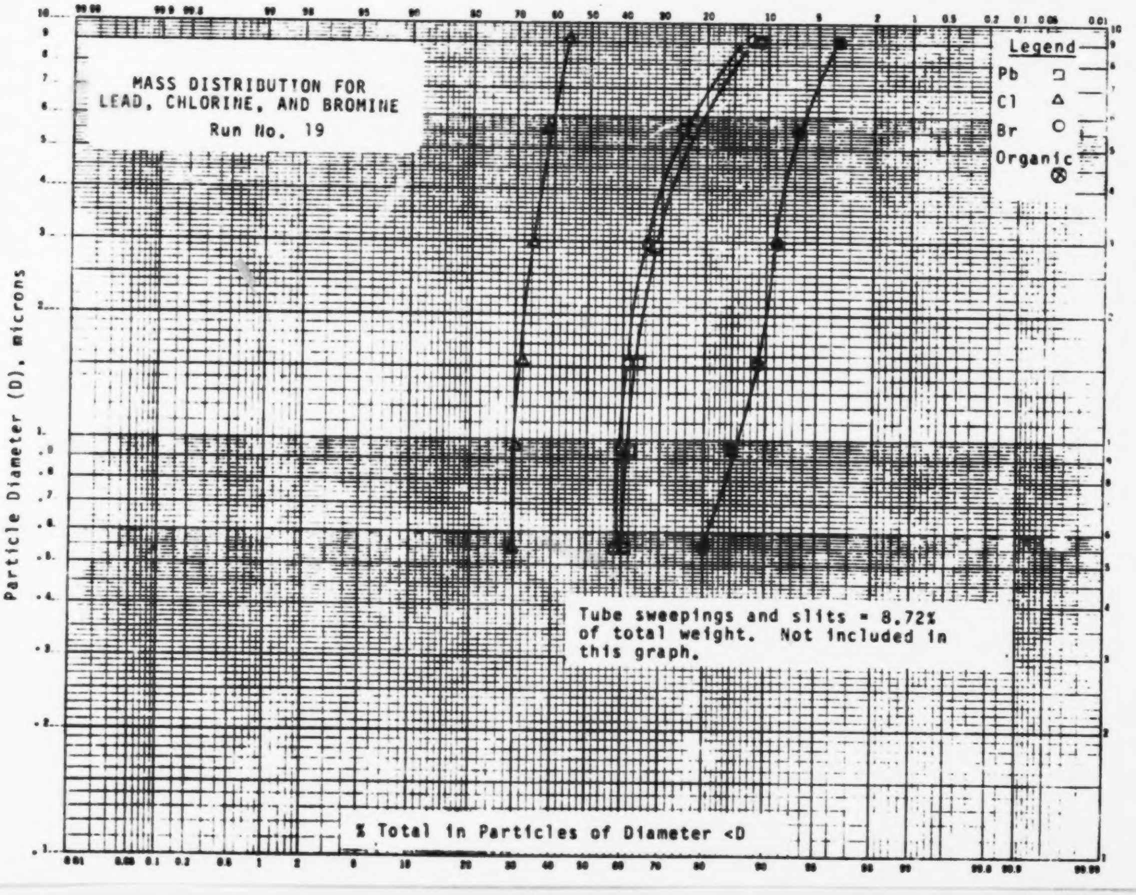

MASS DISTRIBUTION FOR
LEAD, CHLORINE, AND BROMINE
Run 12
Legend
Pb •
Br ○
Cl Δ
Organic □
Particle Diameter (D), microns
% Total in Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99


MASS DISTRIBUTION FOR
LEAD, CHLORINE, AND BROMINE
Run No. 13
Legend
Pb •
Br ○
Cl Δ
Organic □
Particle Diameter (D), microns
% Total in Particles of Diameter <D

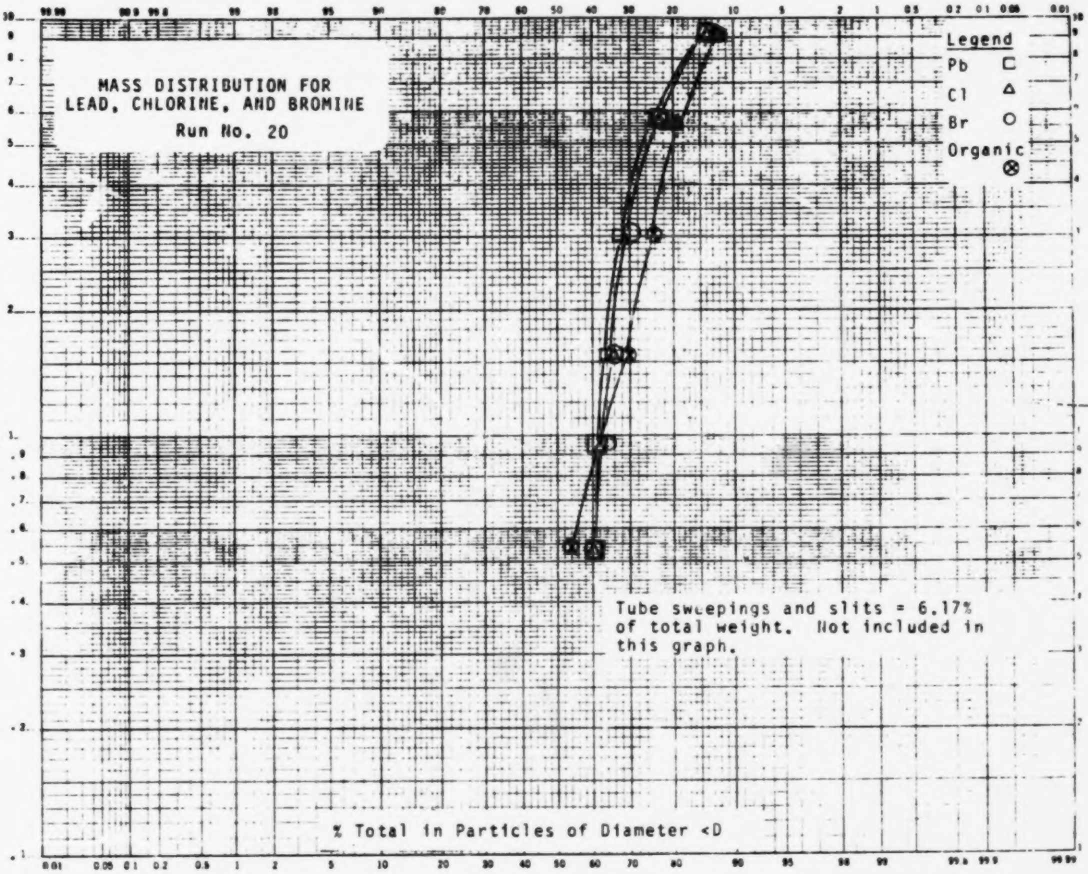

MASS DISTRIBUTION FOR
LEAD, CHLORINE, AND BROMINE
Run No. 14
Legend
Pb •
Br ∘
Organic □
Particle Diameter (D), microns
% Total in Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
.1
.2
.3
.4
.5
.6
.7
.8
.9
1
2
3
4
5
6
7
8
9
10


MASS DISTRIBUTION FOR
LEAD, CHLORINE, AND BROMINE
Run No. 16
Legend
Pb •
Organic ∘
Particle Diameter (D), microns
% Total in Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
.1
.2
.3
.4
.5
.6
.7
.8
.9
1
2
3
4
5
6
7
8
9
10



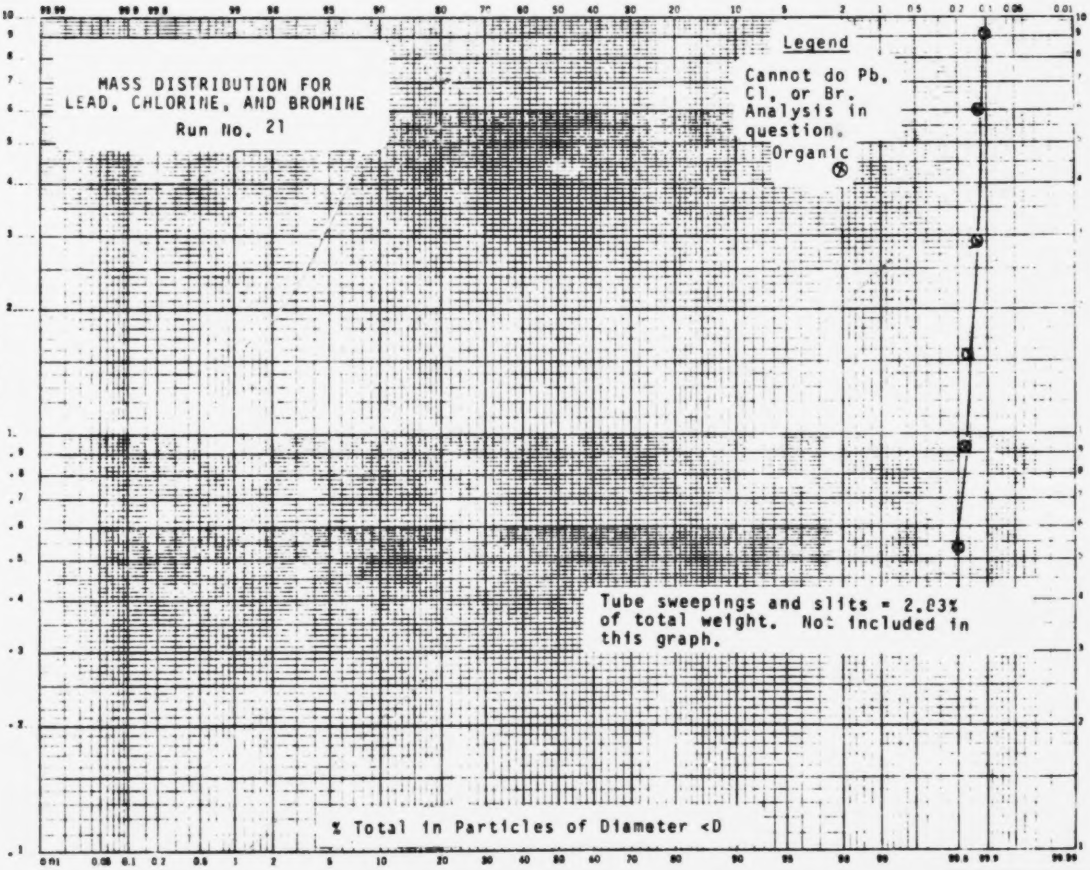


Tube sweepings and slits = 8.72% of total weight. Not included in this graph.



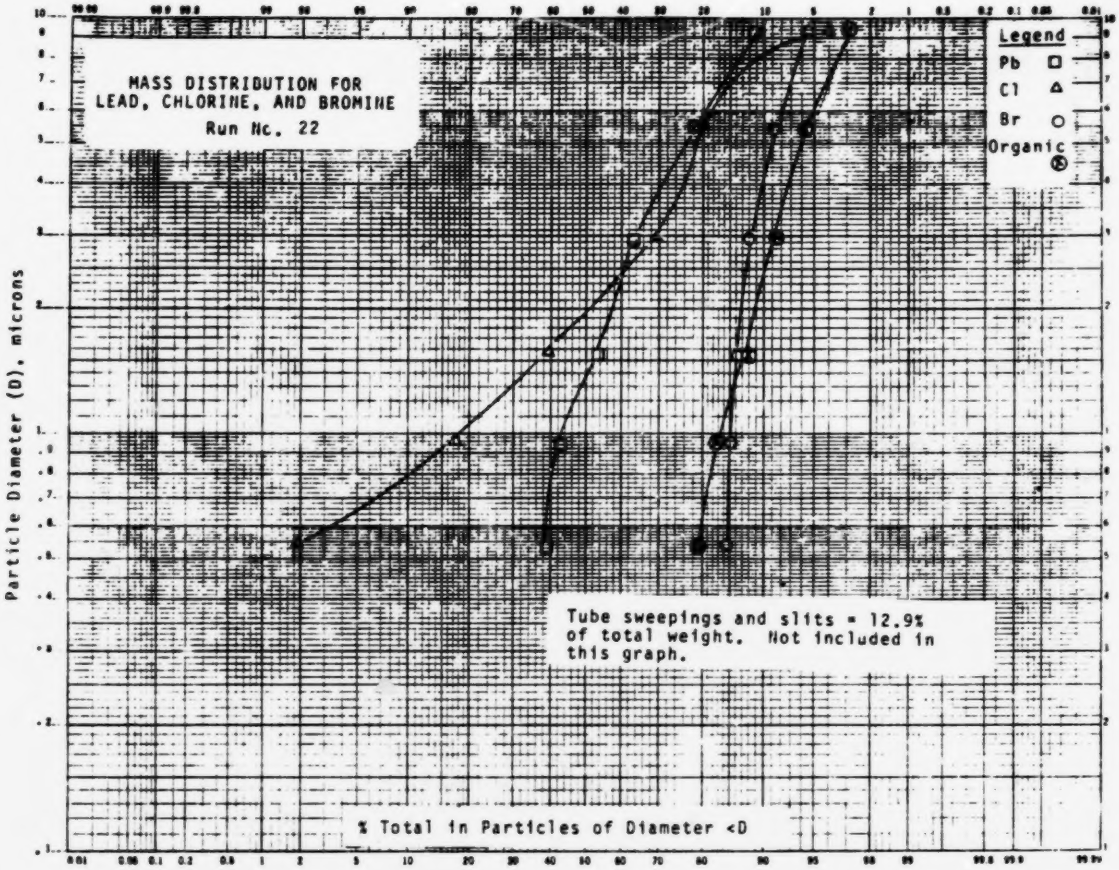
MASS DISTRIBUTION FOR
LEAD, CHLORINE, AND BROMINE
Run No. 20

Tube sweepings and slits = 6.17% of total weight. Not included in this graph.



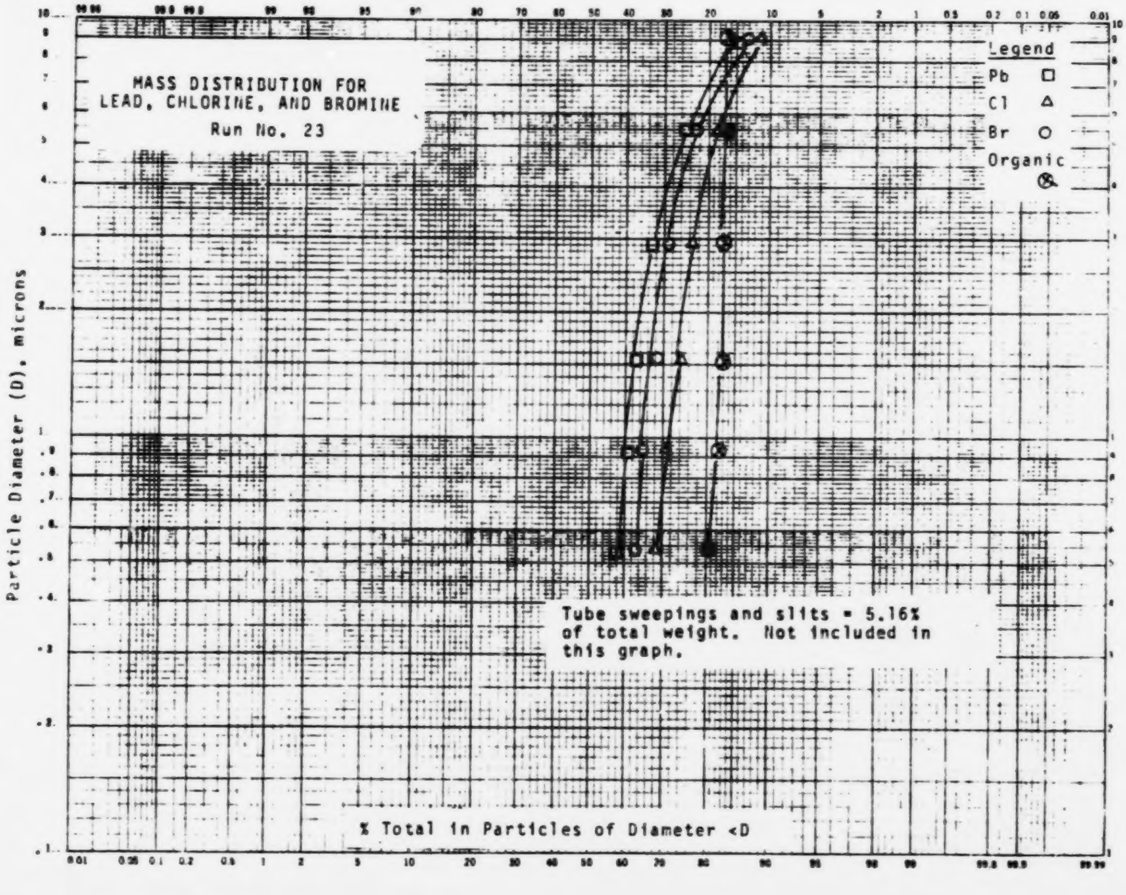
MASS DISTRIBUTION FOR
LEAD, CHLORINE, AND BROMINE
Run No. 21

Tube sweepings and slits = 2.03% of total weight. Not included in this graph.



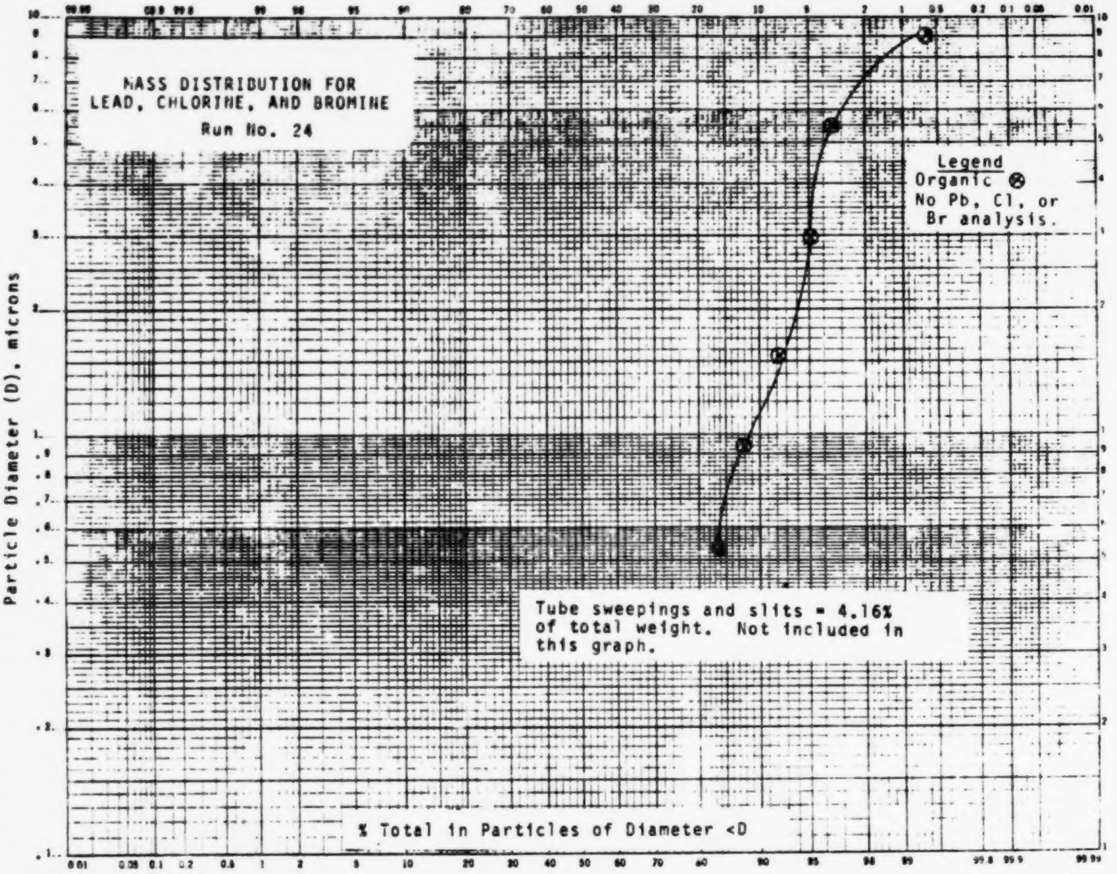
MASS DISTRIBUTION FOR
LEAD, CHLORINE, AND BROMINE
Run No. 22

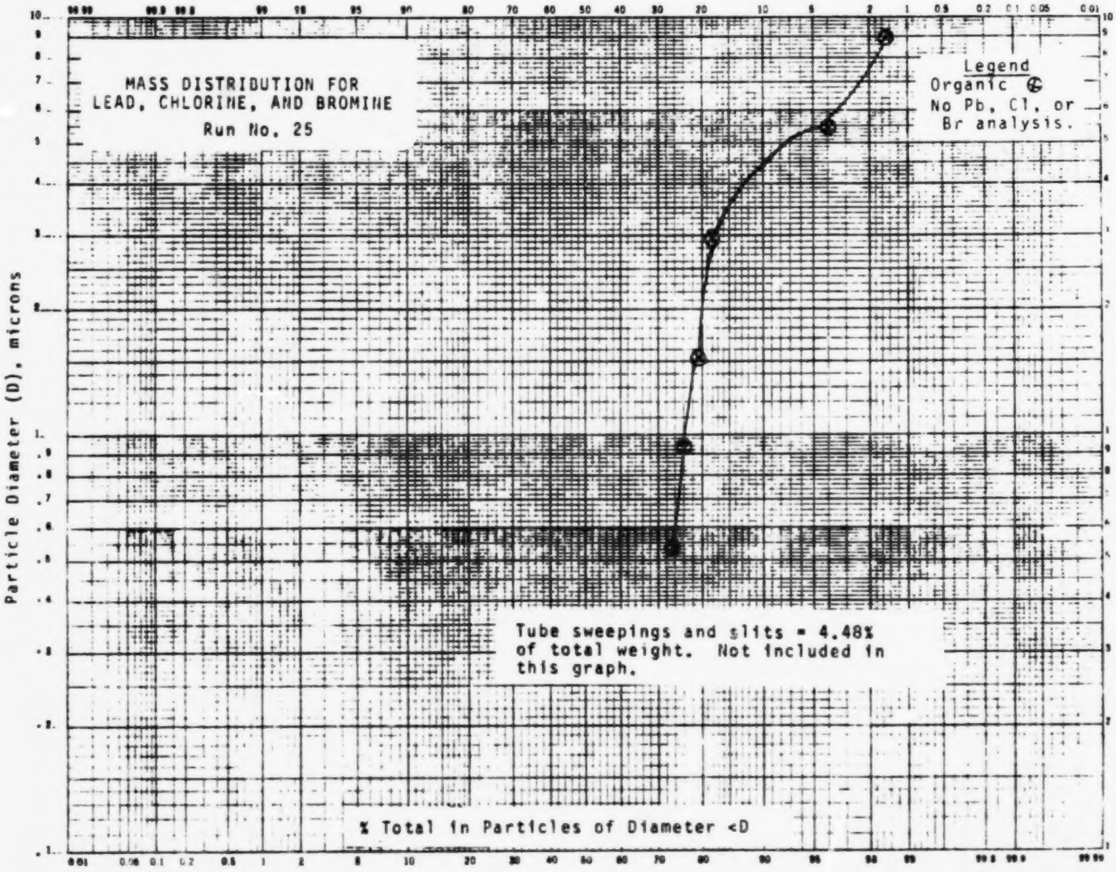
Tube sweepings and slits = 12.9% of total weight. Not included in this graph.

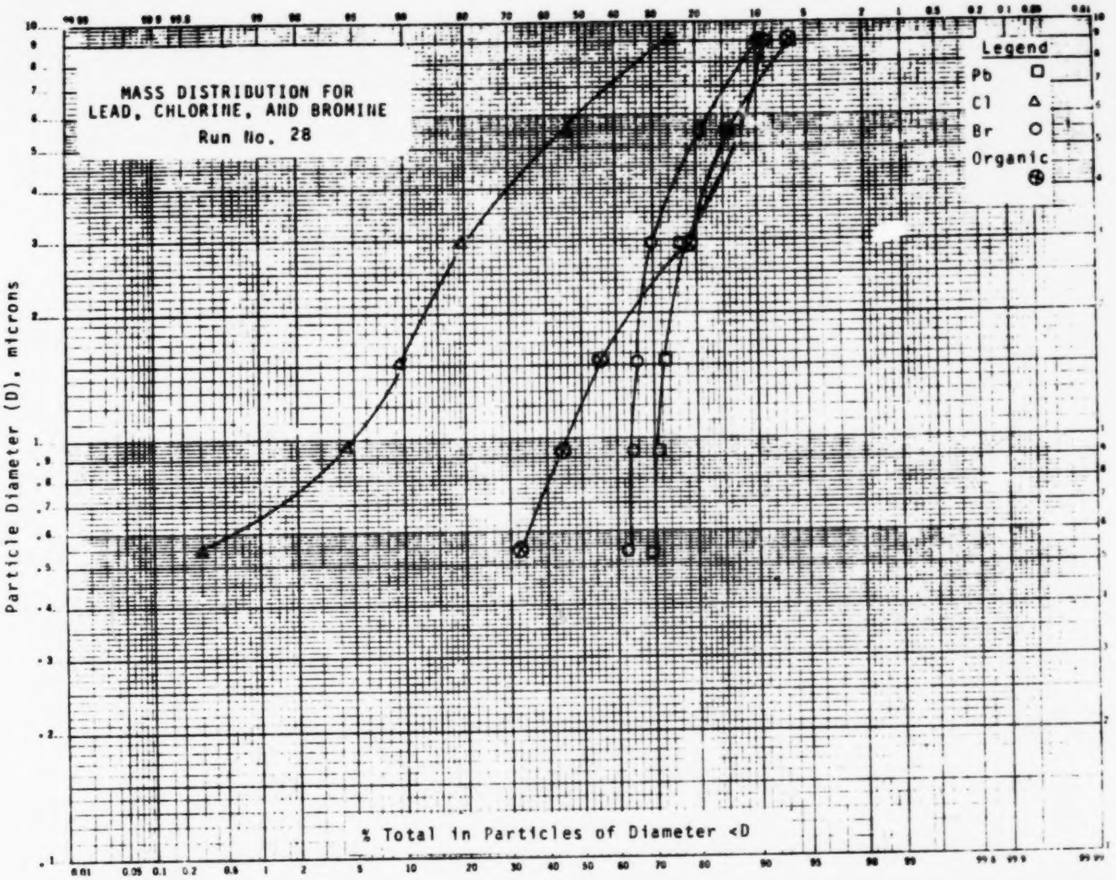


MASS DISTRIBUTION FOR
LEAD, CHLORINE, AND BROMINE
Run No. 23

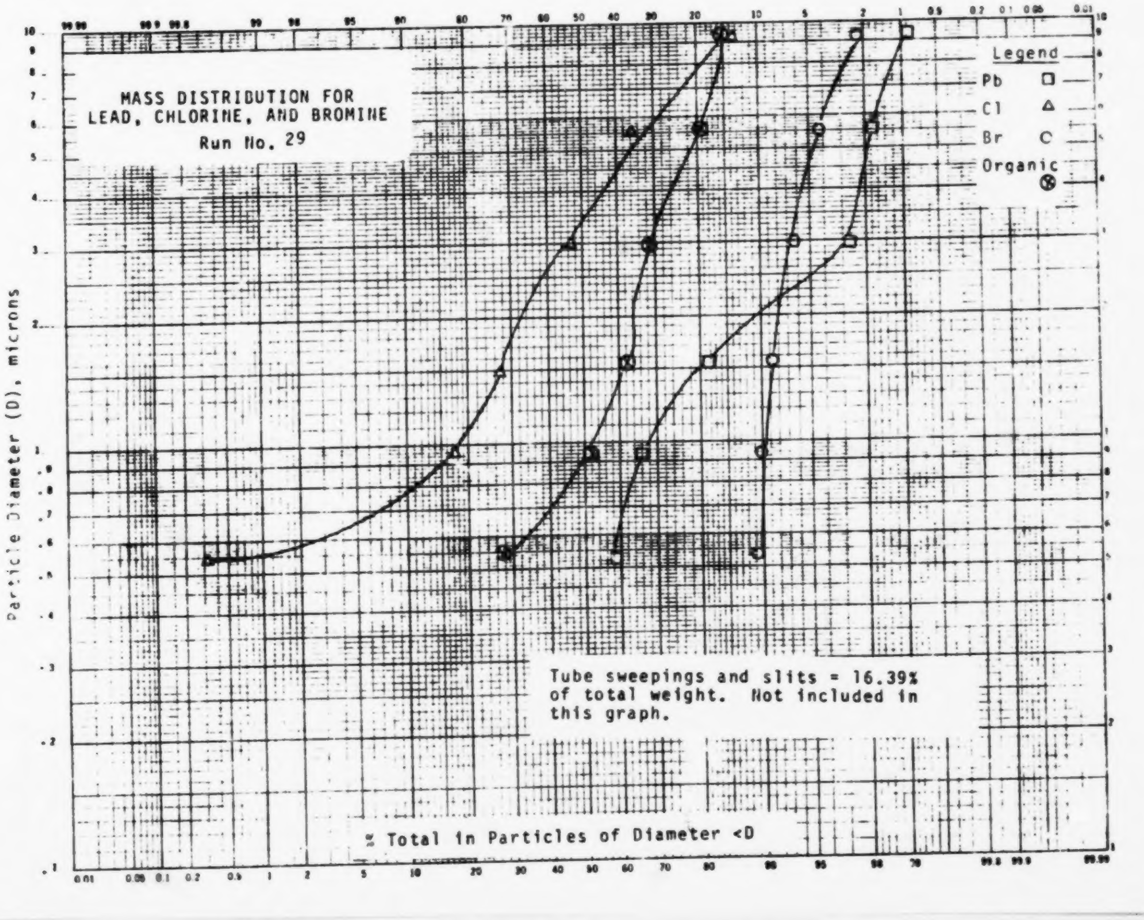
Tube sweepings and slits = 5.16% of total weight. Not included in this graph.


MASS DISTRIBUTION FOR
LEAD, CHLORINE, AND BROMINE
Run No. 24
Legend
Organic ⊗
No Pb, Cl, or
Br analysis.
Tube sweepings and slits = 4.16%
of total weight. Not included in
this graph.
Particle Diameter (D), microns
% Total in Particles of Diameter <D


MASS DISTRIBUTION FOR
LEAD, CHLORINE, AND BROMINE
Run No. 25
Legend
Organic ⊗
No Pb, Cl, or
Br analysis.
Tube sweepings and slits = 4.48%
of total weight. Not included in
this graph.
Particle Diameter (D), microns
% Total in Particles of Diameter <D

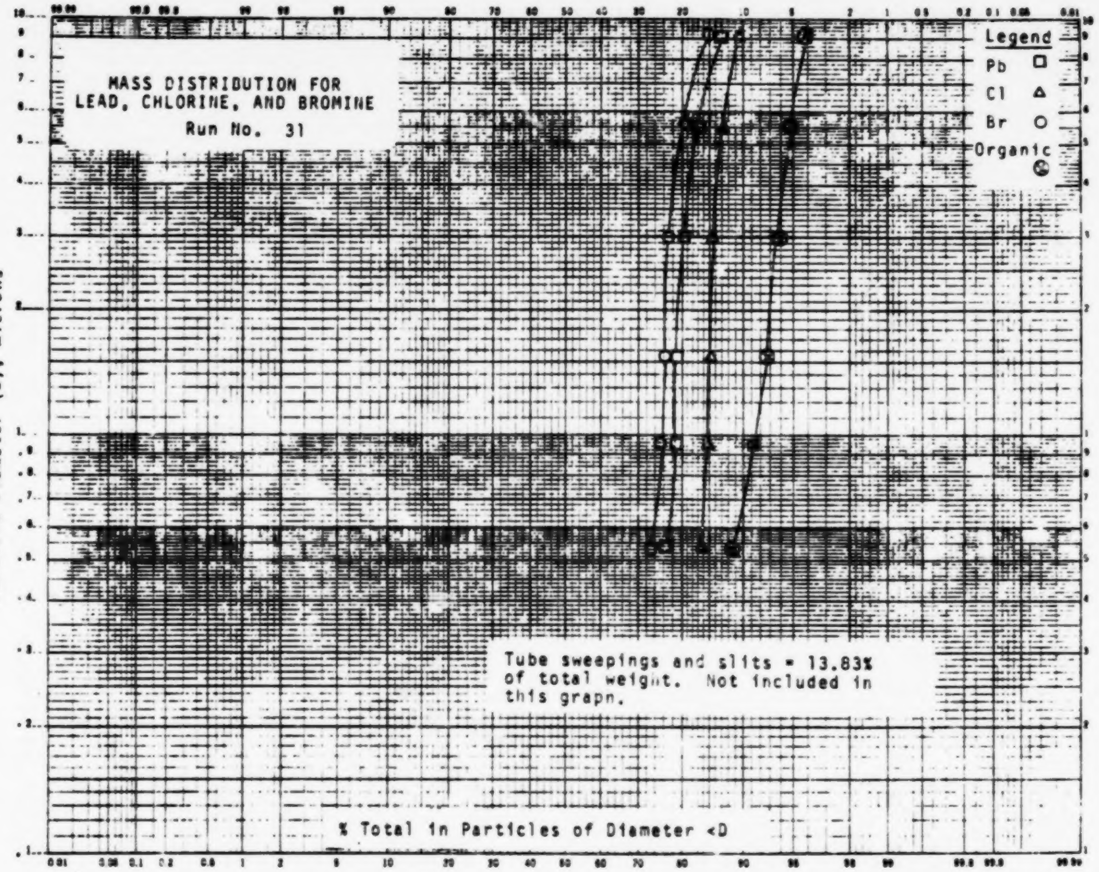


MASS DISTRIBUTION FOR LEAD, CHLORINE, AND BROMINE
Run No. 28

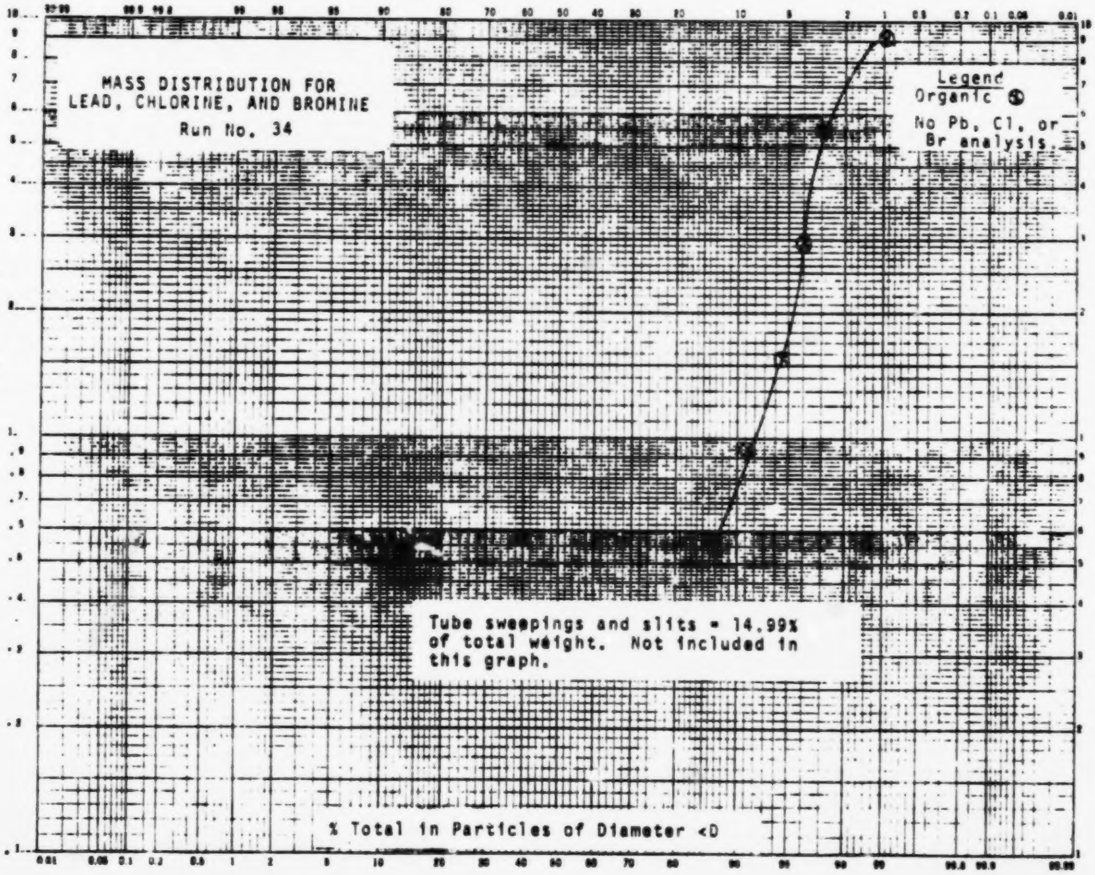


MASS DISTRIBUTION FOR LEAD, CHLORINE, AND BROMINE
Run No. 29

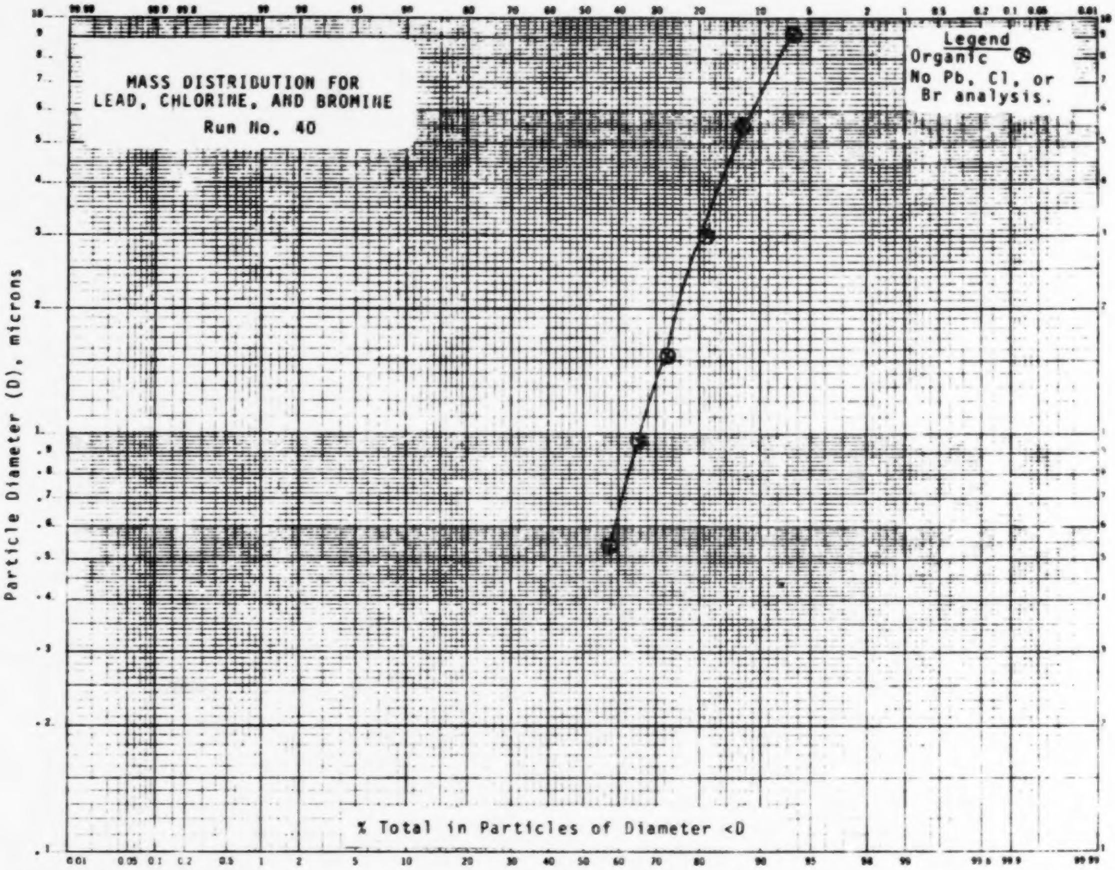
Tube sweepings and slits = 16.39% of total weight. Not included in this graph.


MASS DISTRIBUTION FOR LEAD, CHLORINE, AND BROMINE
Run No. 31

Tube sweepings and slits = 13.83% of total weight. Not included in this graph.

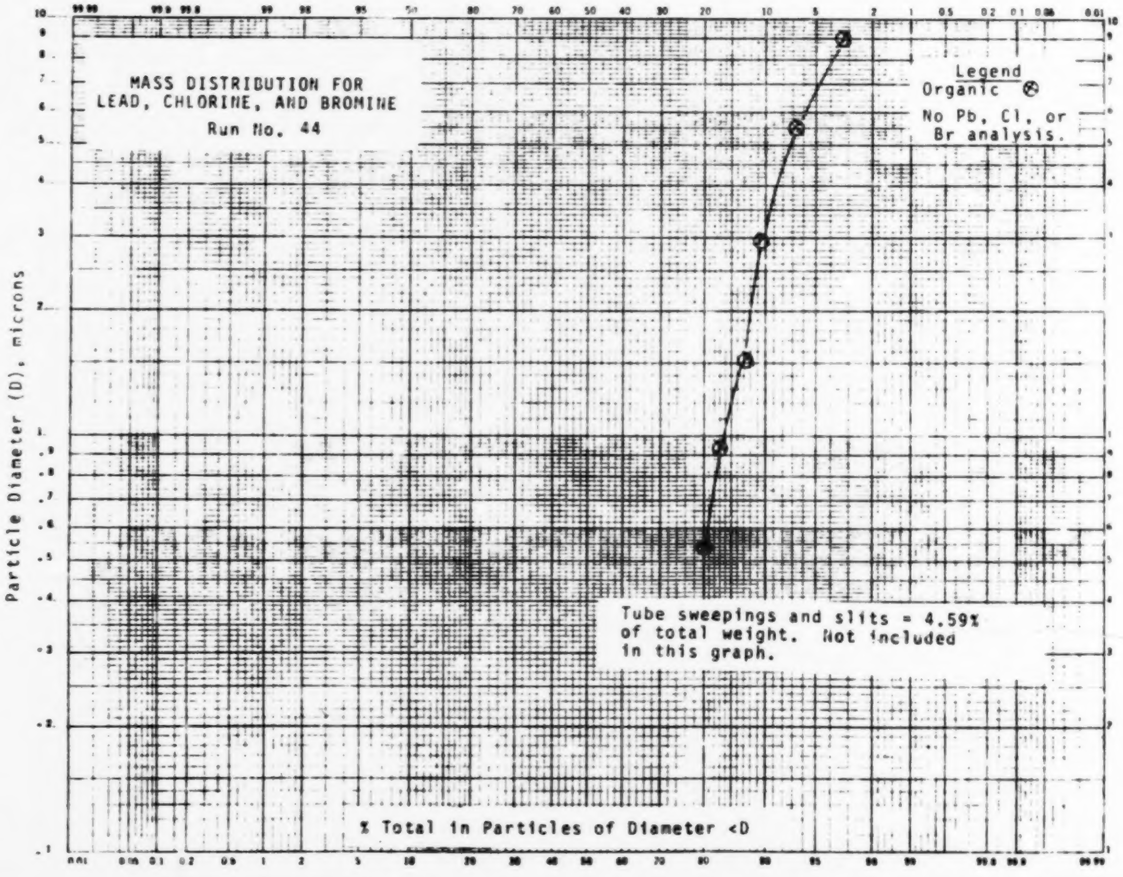

MASS DISTRIBUTION FOR LEAD, CHLORINE, AND BROMINE
Run No. 34

Tube sweepings and slits = 14.99% of total weight. Not included in this graph.



MASS DISTRIBUTION FOR LEAD, CHLORINE, AND BROMINE
Run No. 40

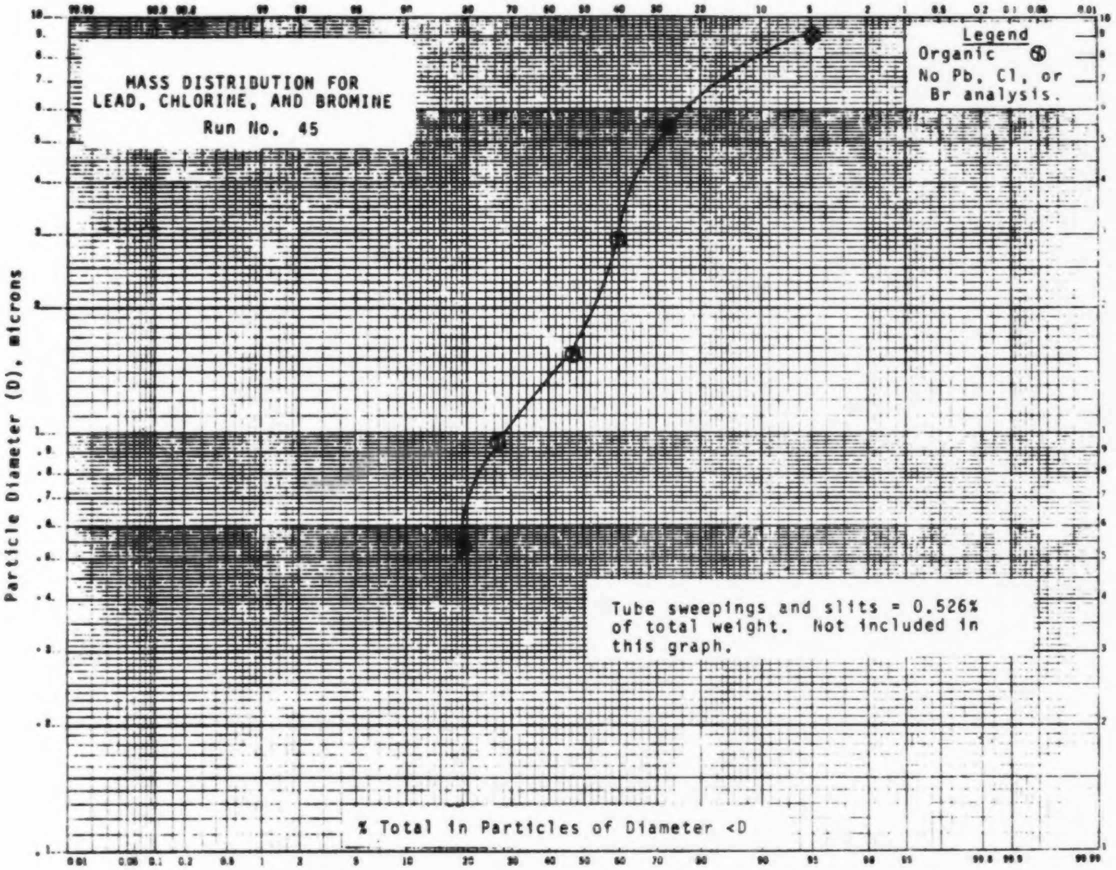
Legend
Organic ⊗
No Pb, Cl, or Br analysis.



MASS DISTRIBUTION FOR LEAD, CHLORINE, AND BROMINE
Run No. 44

Legend
Organic ⊗
No Pb, Cl, or Br analysis.

Tube sweepings and slits = 4.59% of total weight. Not included in this graph.

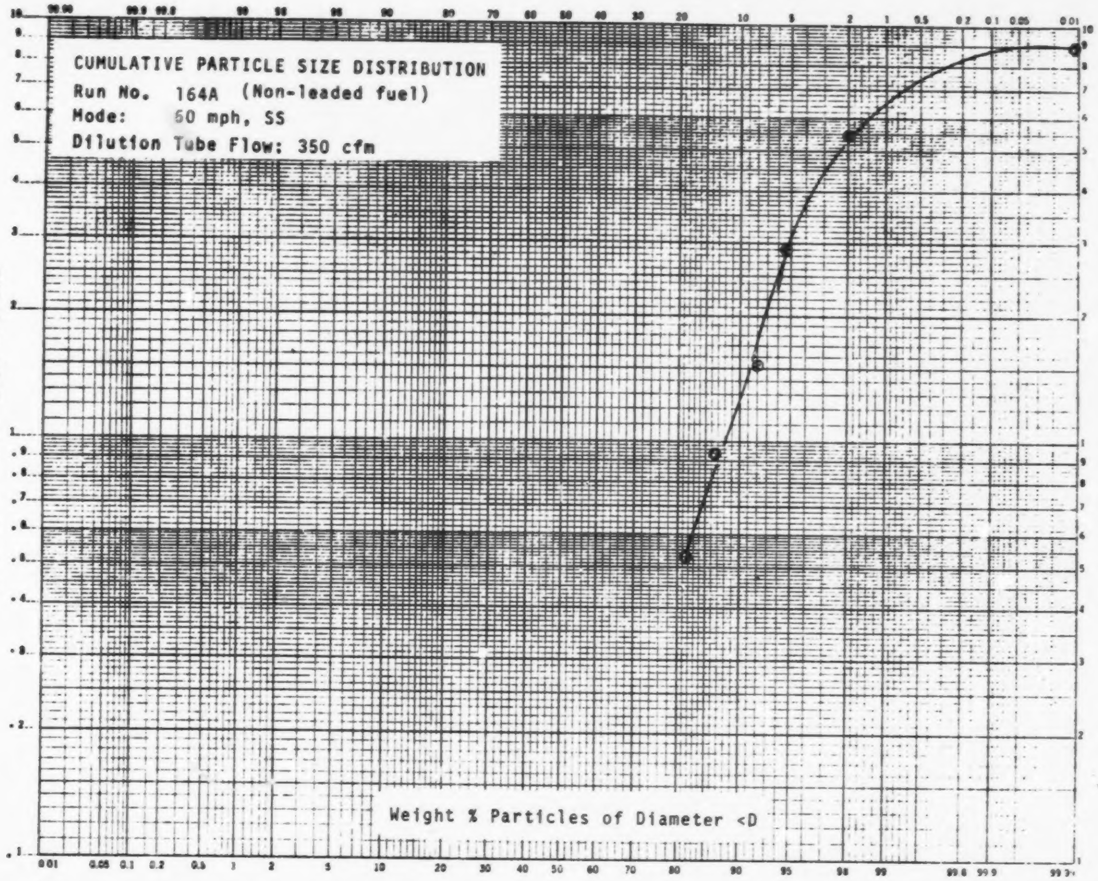


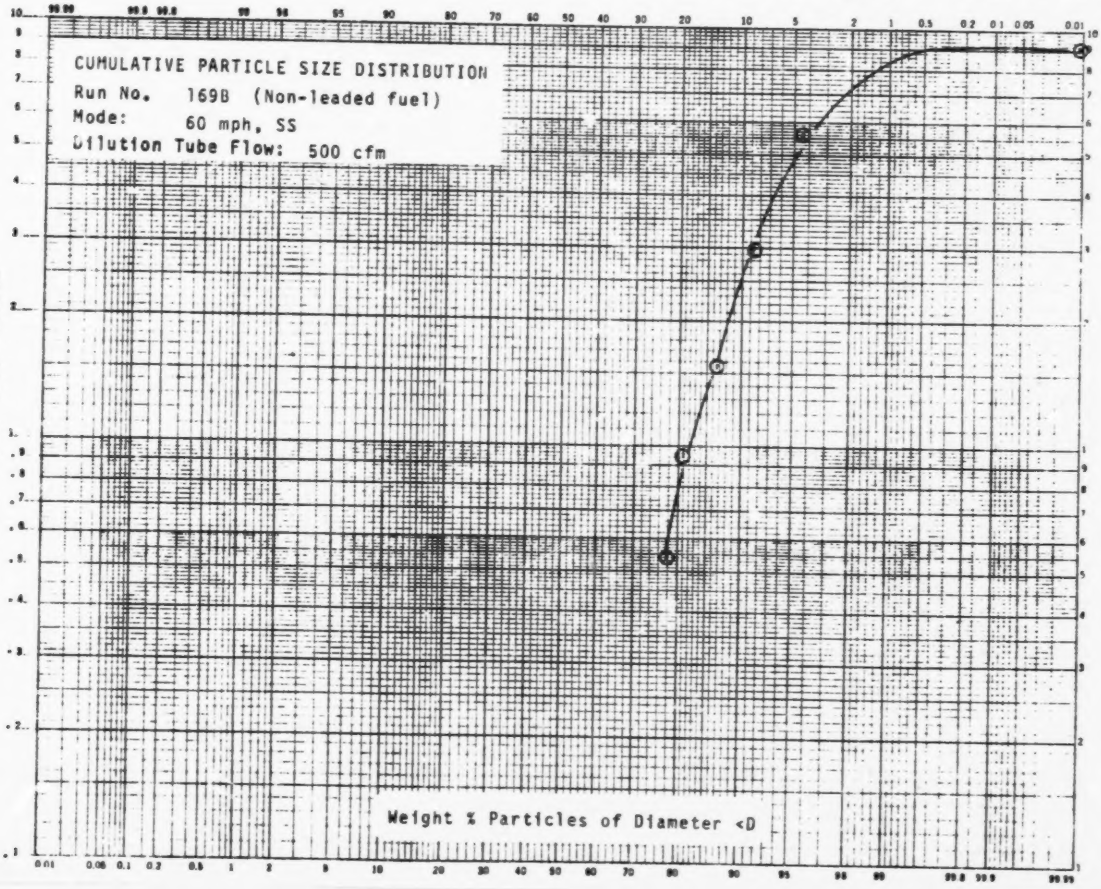
MASS DISTRIBUTION FOR
LEAD, CHLORINE, AND BROMINE
Run No. 45

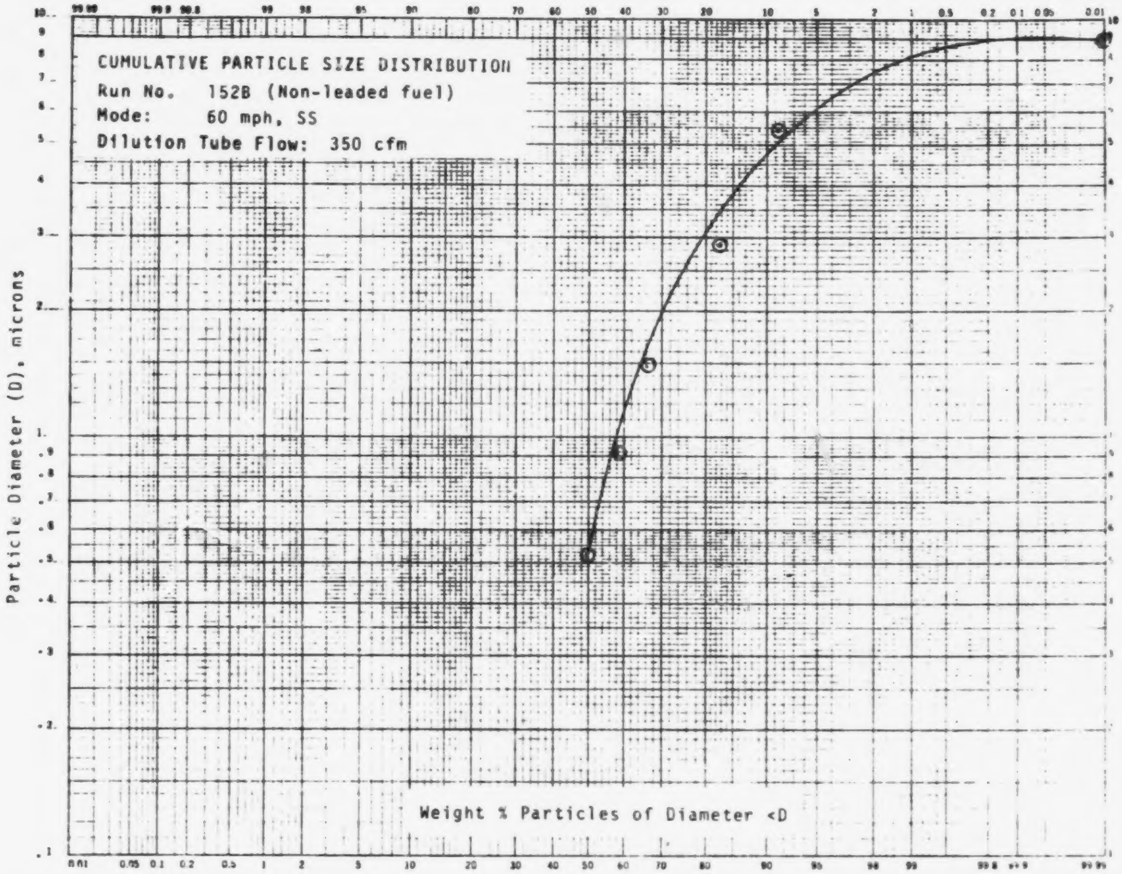
Tube sweepings and slits = 0.526% of total weight. Not included in this graph.

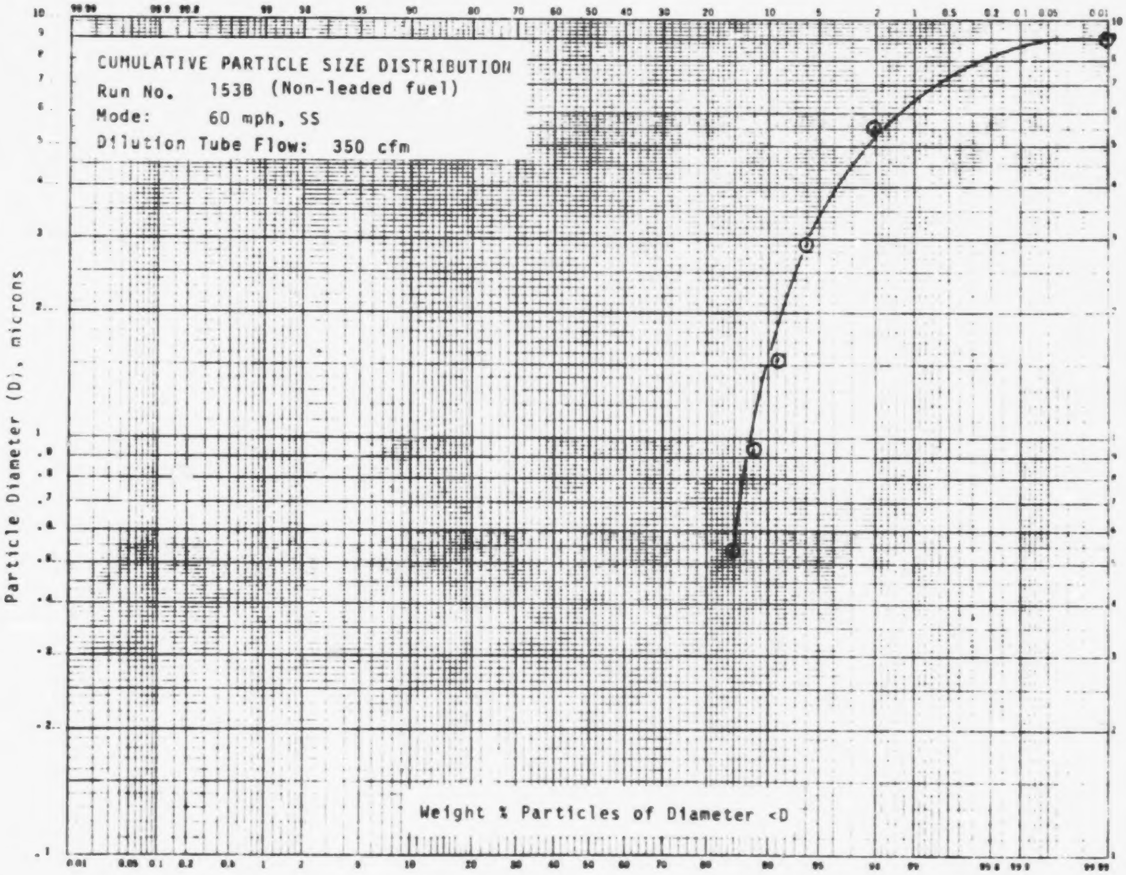
APPENDIX D

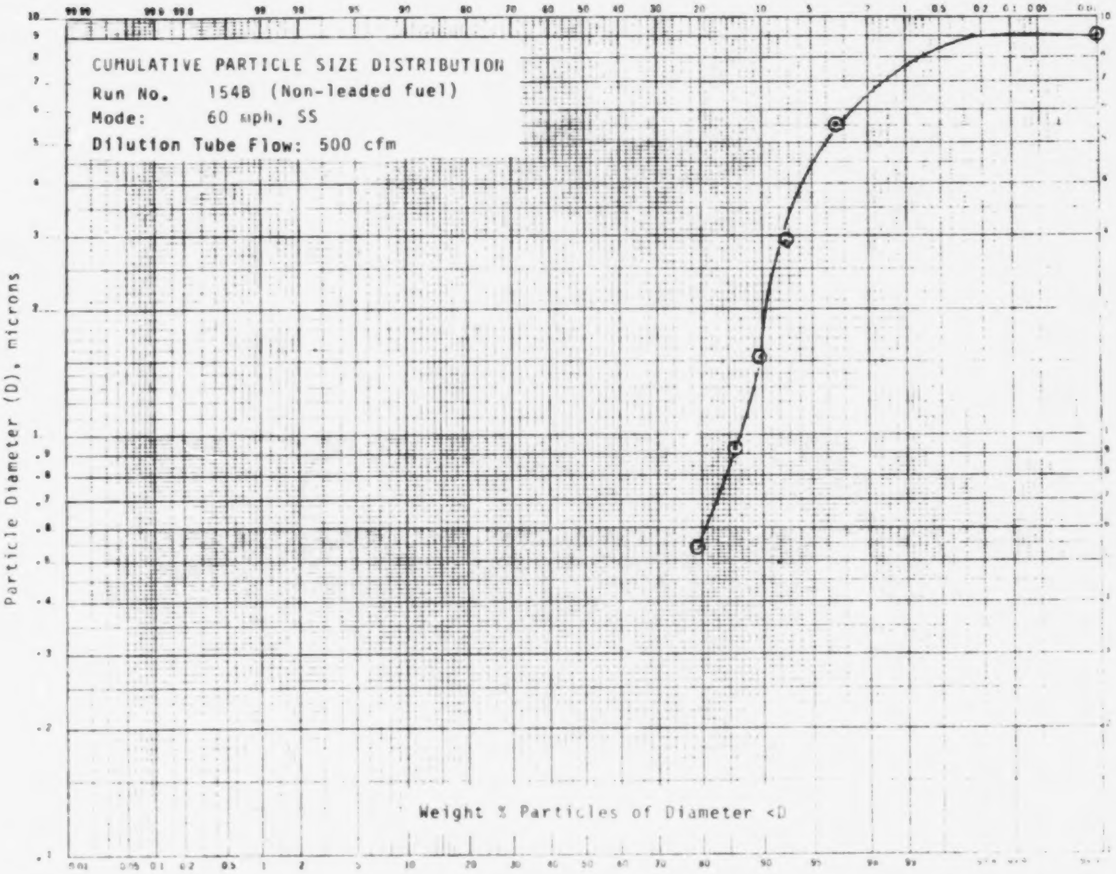
Cumulative Particle Size Distribution of Particulate and of Lead

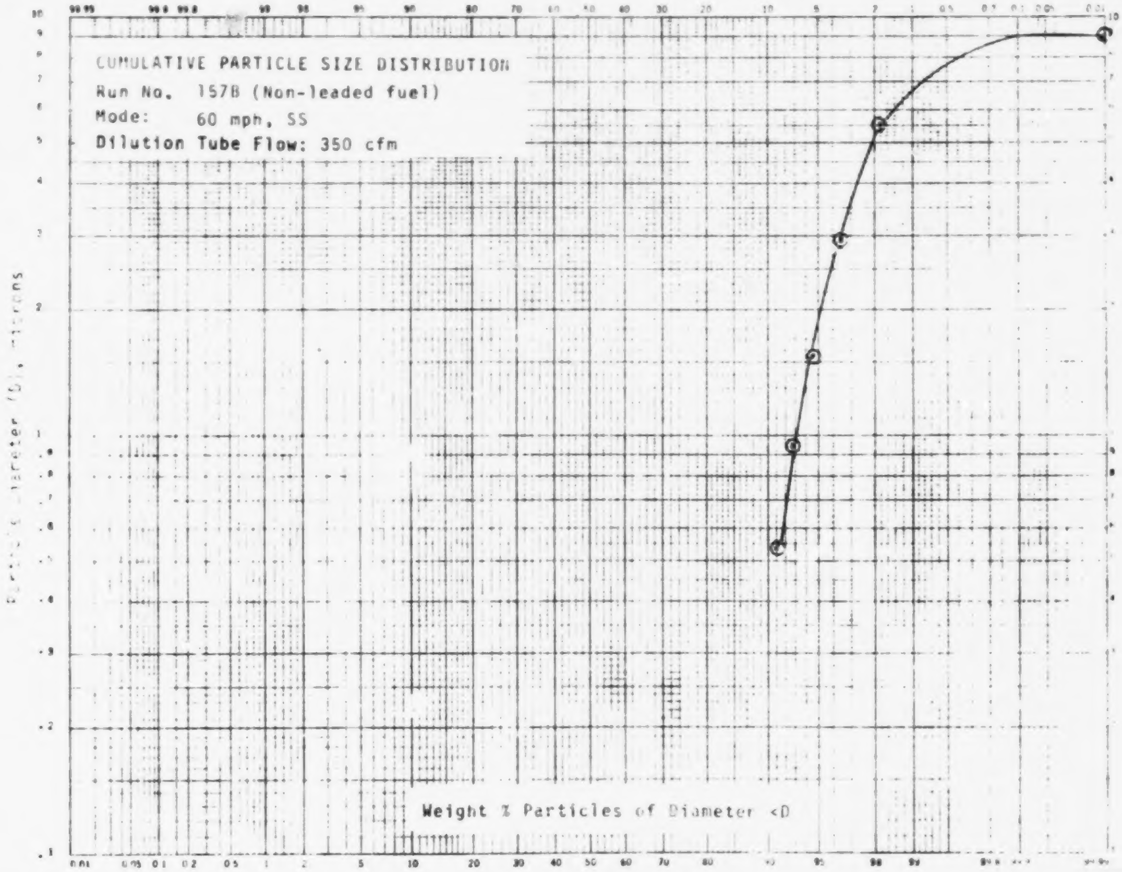

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 164A (Non-leaded fuel)
Mode: 60 mph, SS
Dilution Tube Flow: 350 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D

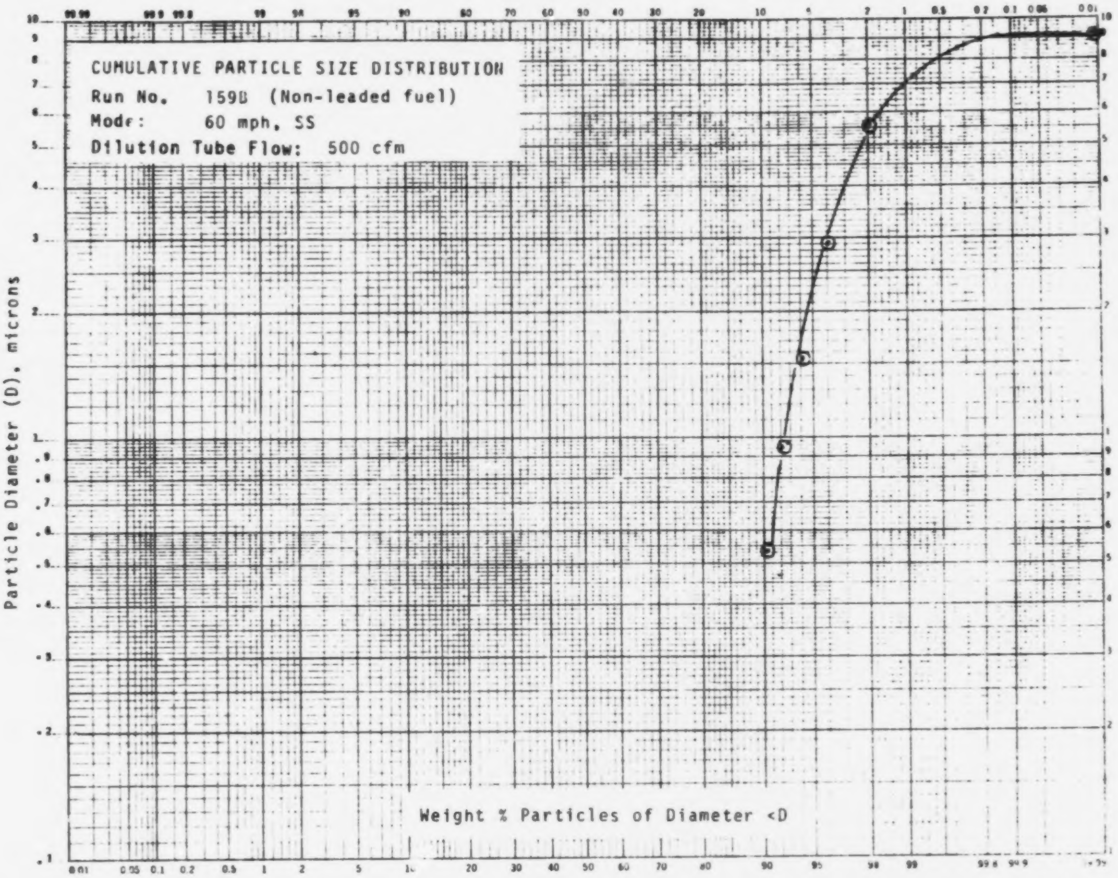

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 169B (Non-leaded fuel)
Mode: 60 mph, SS
Dilution Tube Flow: 500 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D

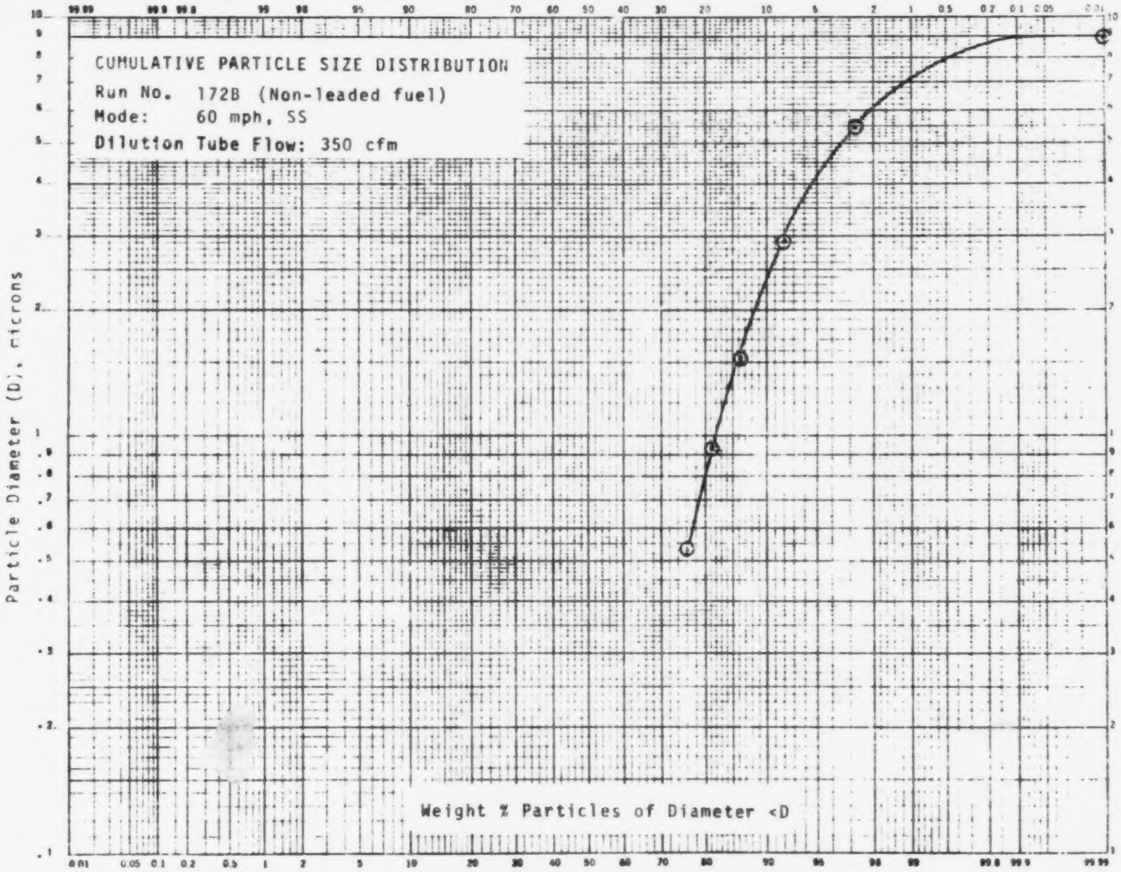

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 152B (Non-leaded fuel)
Mode: 60 mph, SS
Dilution Tube Flow: 350 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D
99.99 99.9 99.8 99 98 95 90 80 70 60 50 40 30 20 10 5 2 1 0.5 0.2 0.1 0.05 0.01
0.01 0.05 0.1 0.2 0.5 1 2 5 10 20 30 40 50 60 70 80 90 95 98 99 99.8 99.9 99.99
10 9 8 7 6 5 4 3 2 1 .9 .8 .7 .6 .5 .4 .3 .2 .1

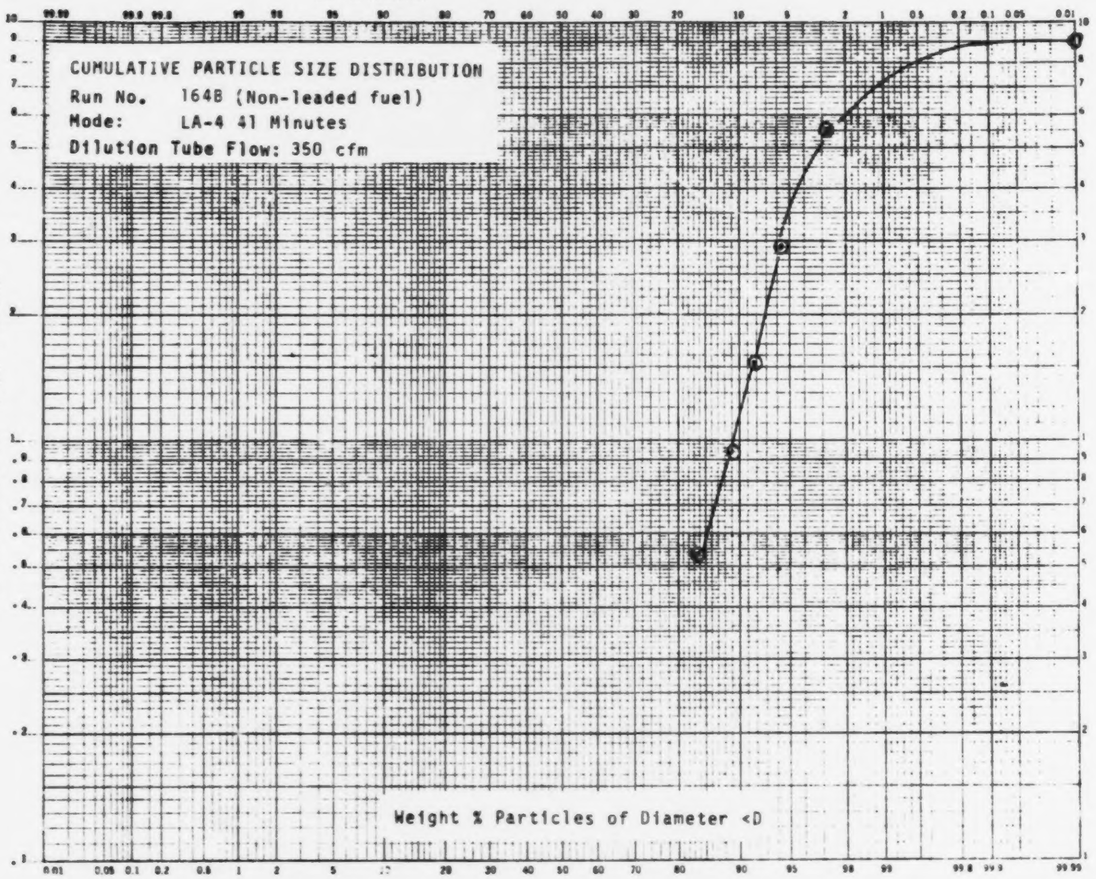

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 153B (Non-leaded fuel)
Mode: 60 mph, SS
Dilution Tube Flow: 350 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D
99.99 99.9 99.8 99 98 95 90 80 70 60 50 40 30 20 10 5 2 1 0.5 0.2 0.1 0.05 0.01
0.01 0.05 0.1 0.2 0.5 1 2 5 10 20 30 40 50 60 70 80 90 95 98 99 99.8 99.9 99.99
10 9 8 7 6 5 4 3 2 1 .9 .8 .7 .6 .5 .4 .3 .2 .1

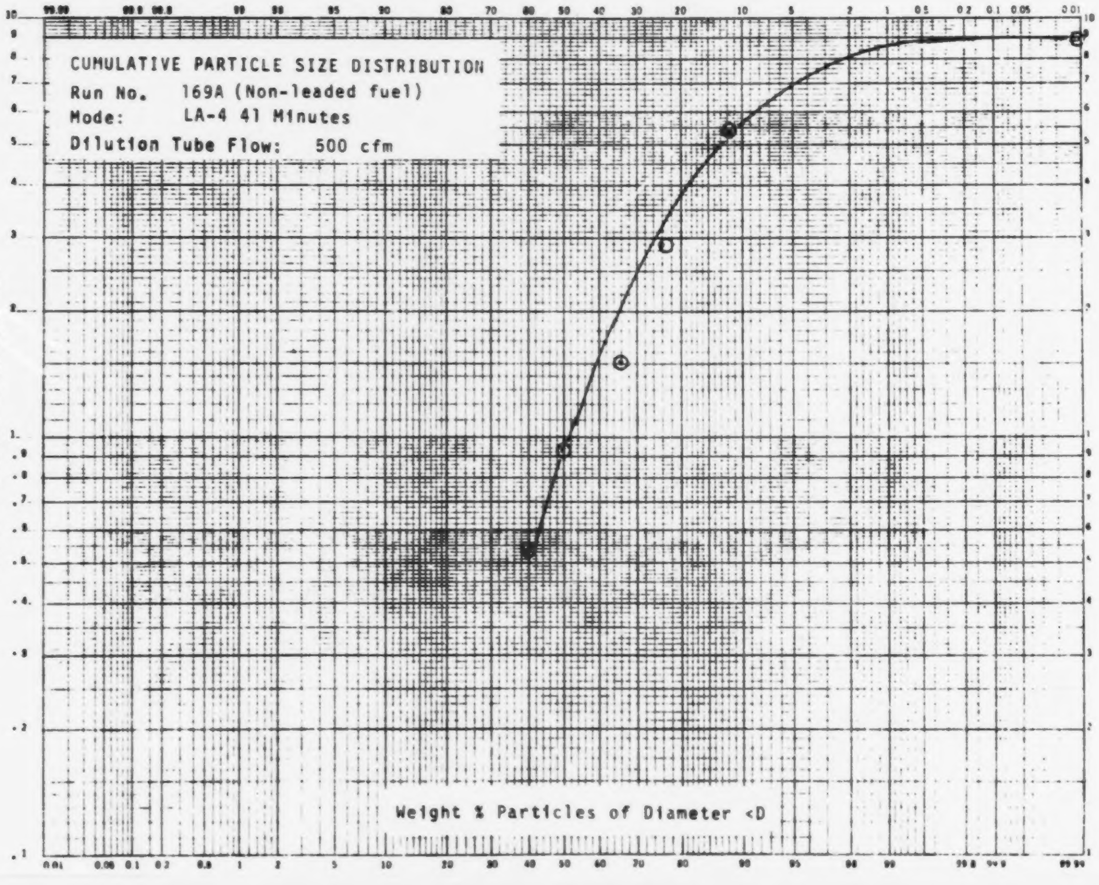

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 154B (Non-leaded fuel)
Mode: 60 mph, SS
Dilution Tube Flow: 500 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.99
99.9
99.8
99
98
95
90
80
70
60
50
40
30
20
10
5
2
1
0.5
0.2
0.1
0.05
0.01

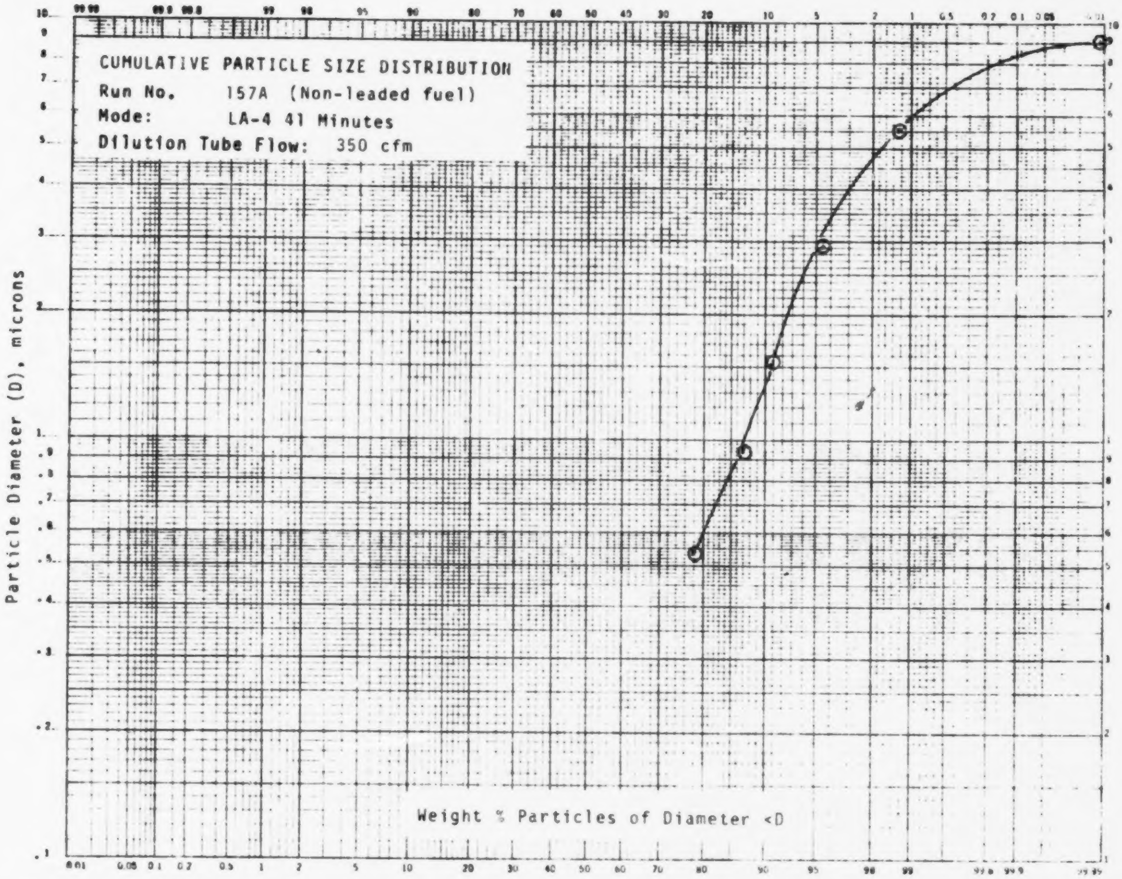

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 157B (Non-leaded fuel)
Mode: 60 mph, SS
Dilution Tube Flow: 350 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.99
99.9
99.8
99
98
95
90
80
70
60
50
40
30
20
10
5
2
1
0.5
0.2
0.1
0.05
0.01

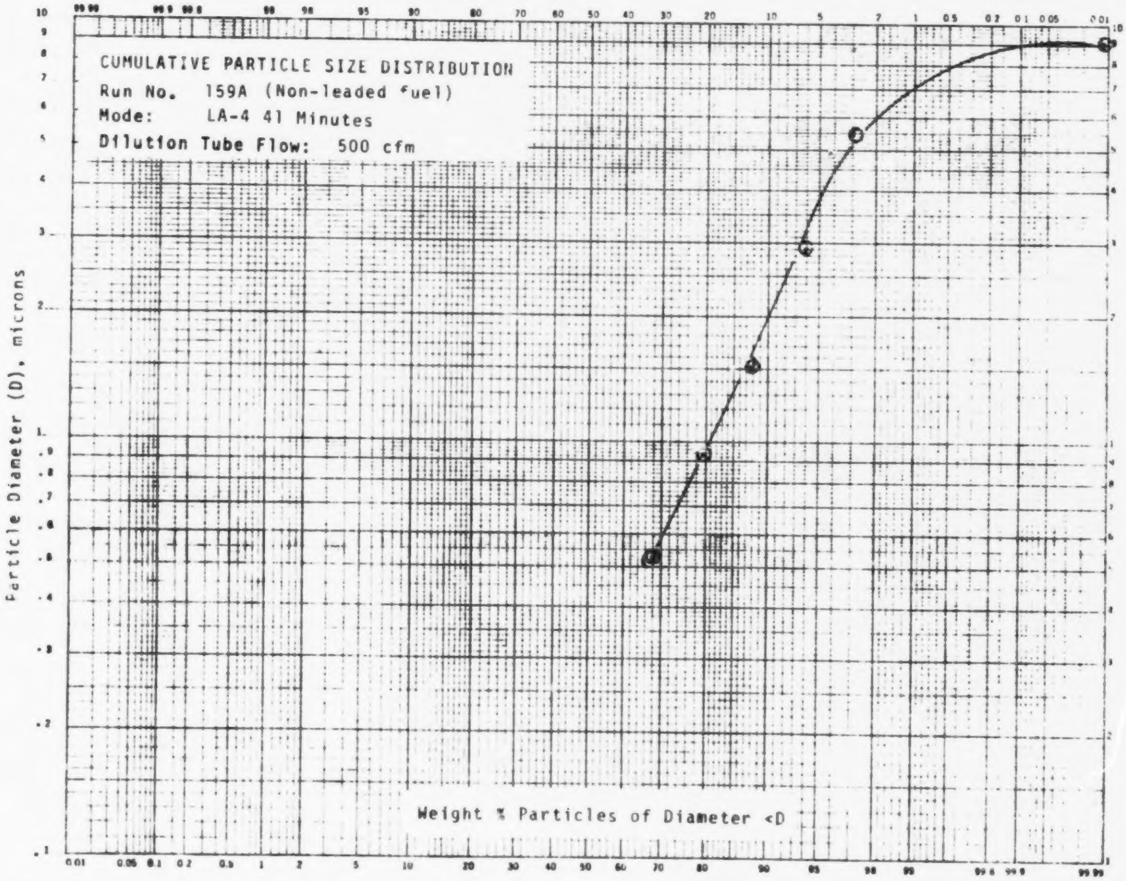

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 159B (Non-leaded fuel)
Mode: 60 mph, SS
Dilution Tube Flow: 500 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99

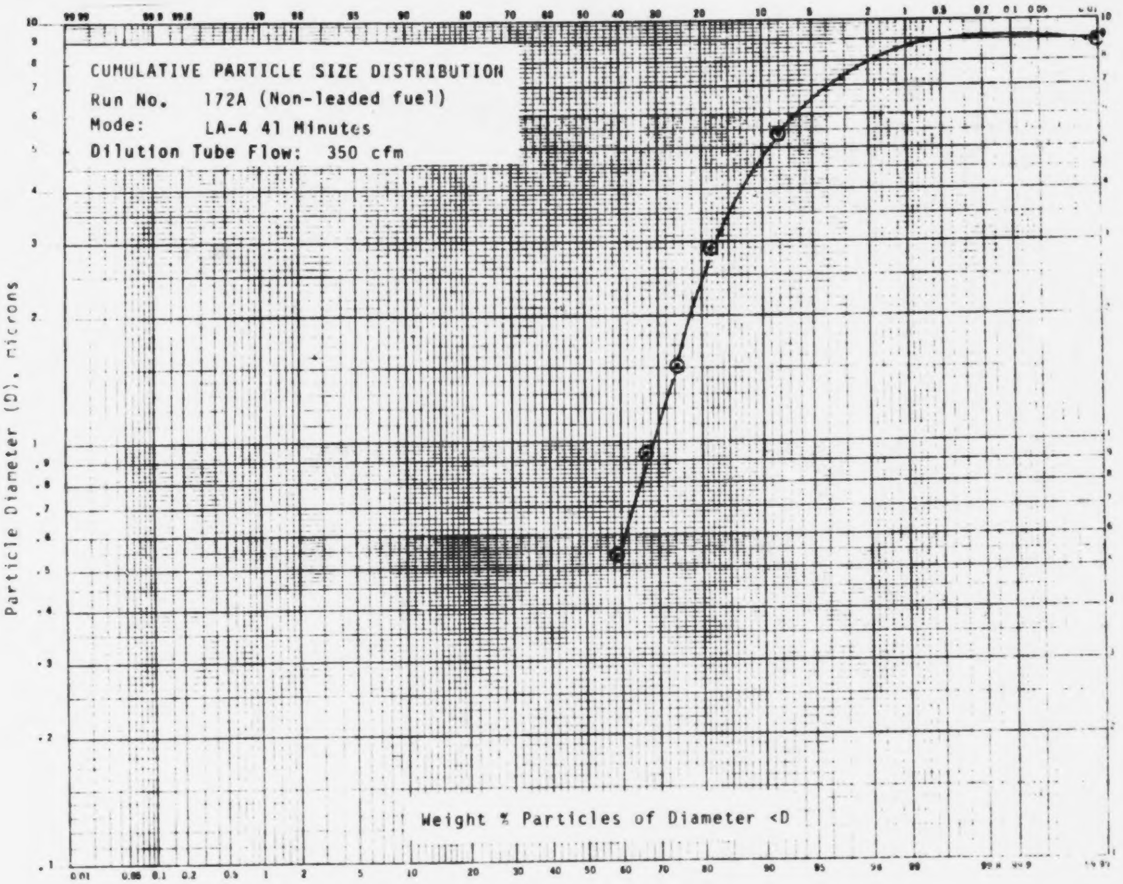

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 172B (Non-leaded fuel)
Mode: 60 mph, SS
Dilution Tube Flow: 350 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99

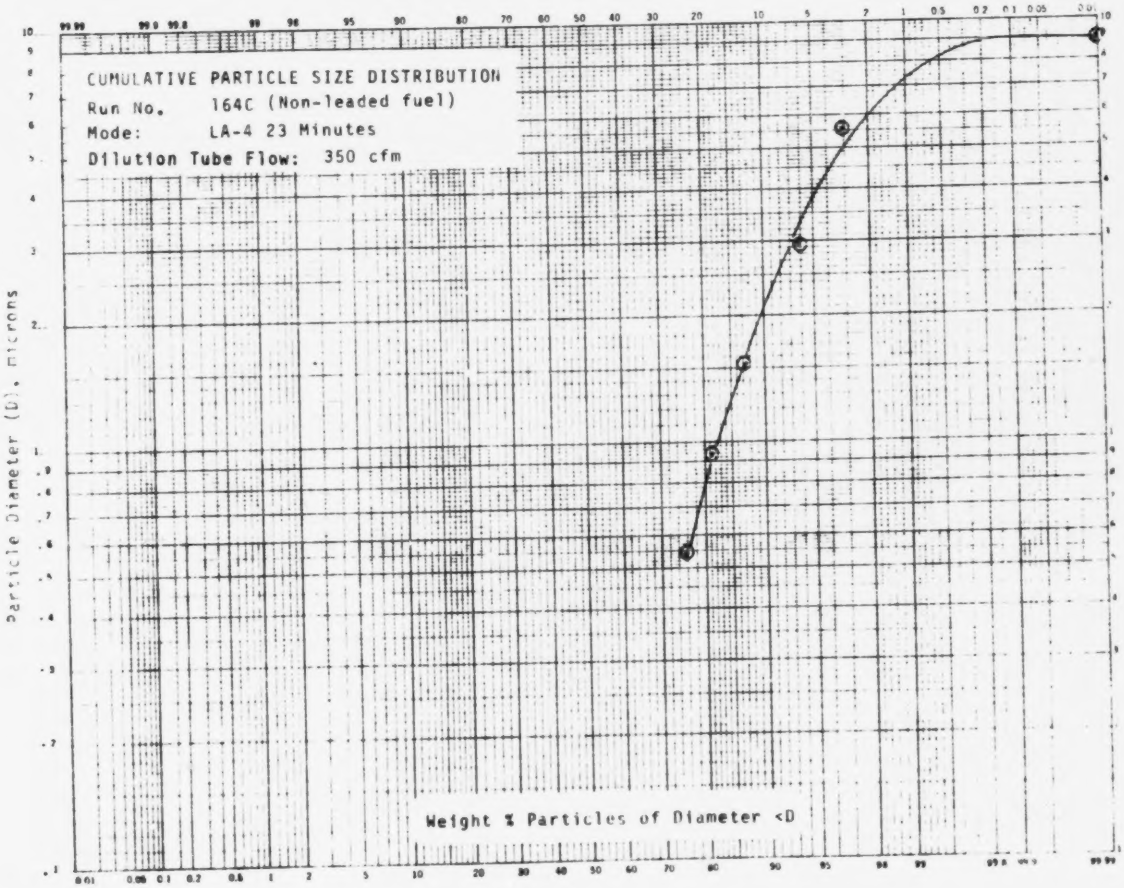

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 164B (Non-leaded fuel)
Mode: LA-4 41 Minutes
Dilution Tube Flow: 350 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D
99.99
99.9
99.8
99
98
95
90
80
70
60
50
40
30
20
10
5
2
1
0.5
0.2
0.1
0.05
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
10
.1

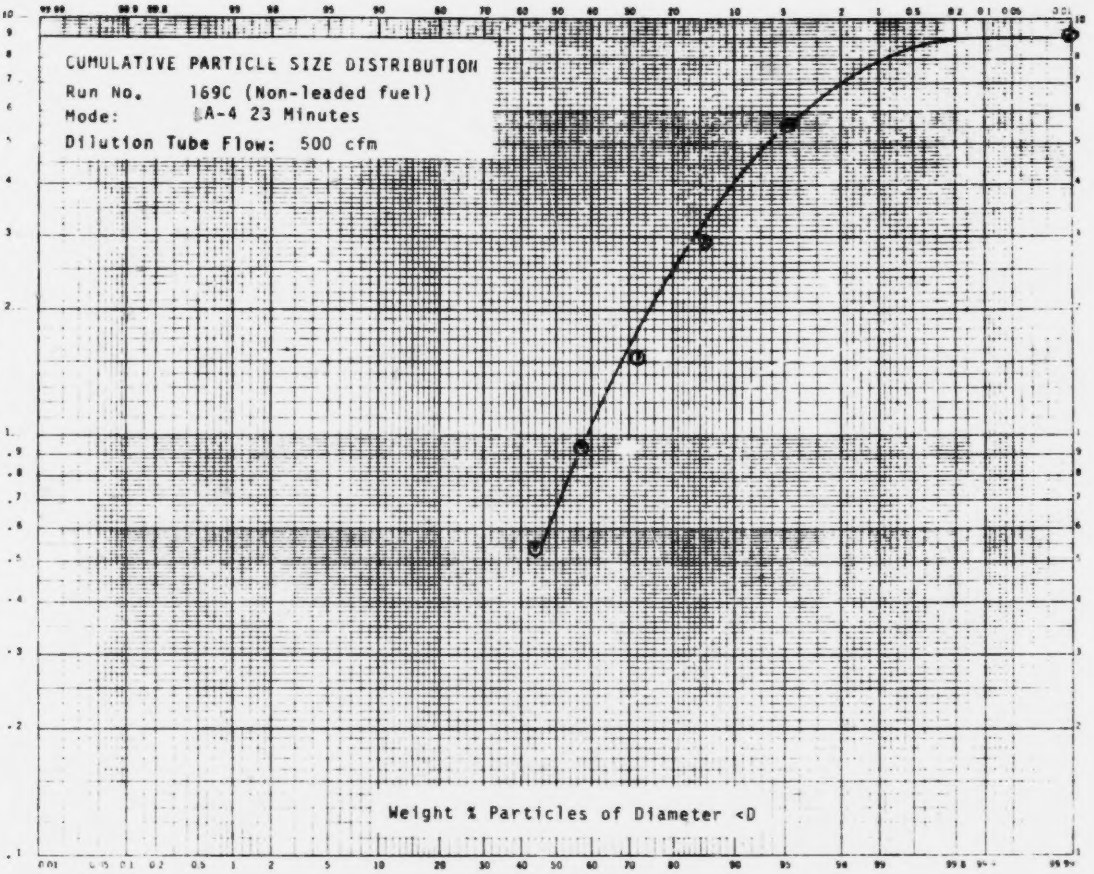

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 169A (Non-leaded fuel)
Mode: LA-4 41 Minutes
Dilution Tube Flow: 500 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D
99.99
99.9
99.8
99
98
95
90
80
70
60
50
40
30
20
10
5
2
1
0.5
0.2
0.1
0.05
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
10
.1

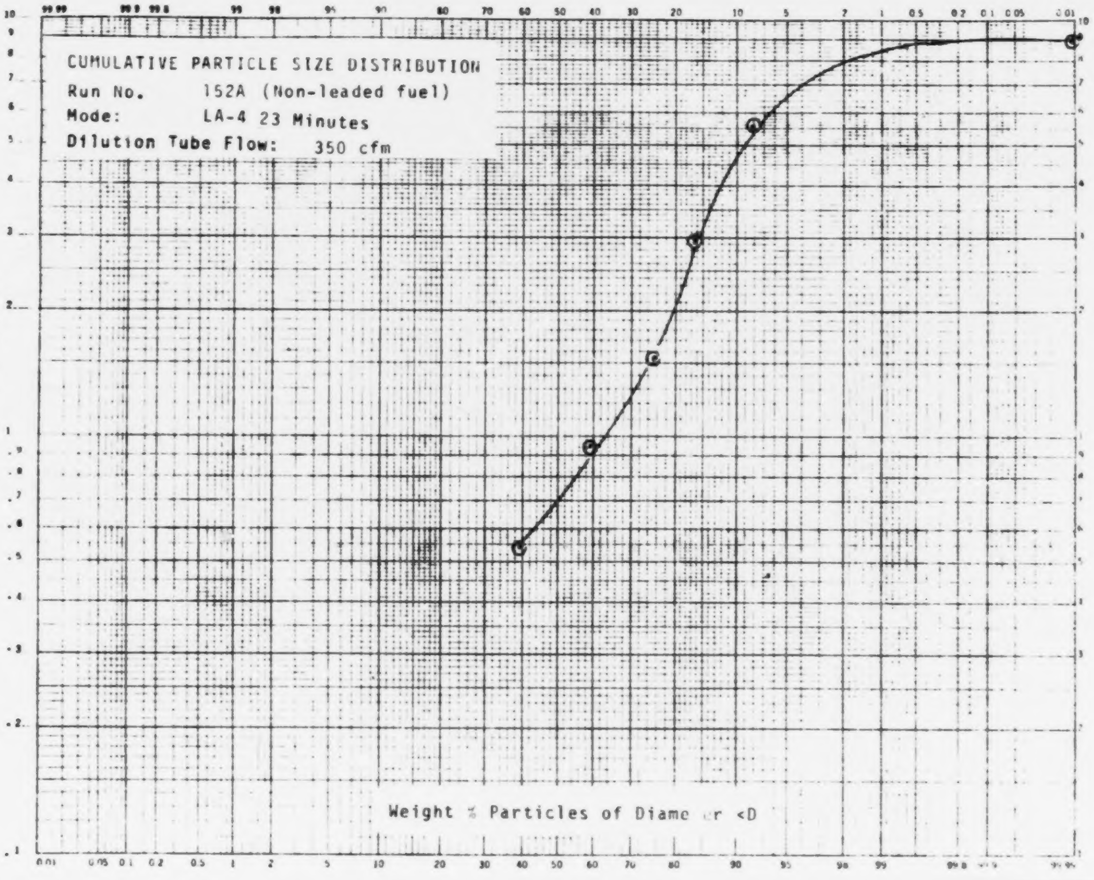

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 157A (Non-leaded fuel)
Mode: LA-4 41 Minutes
Dilution Tube Flow: 350 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99

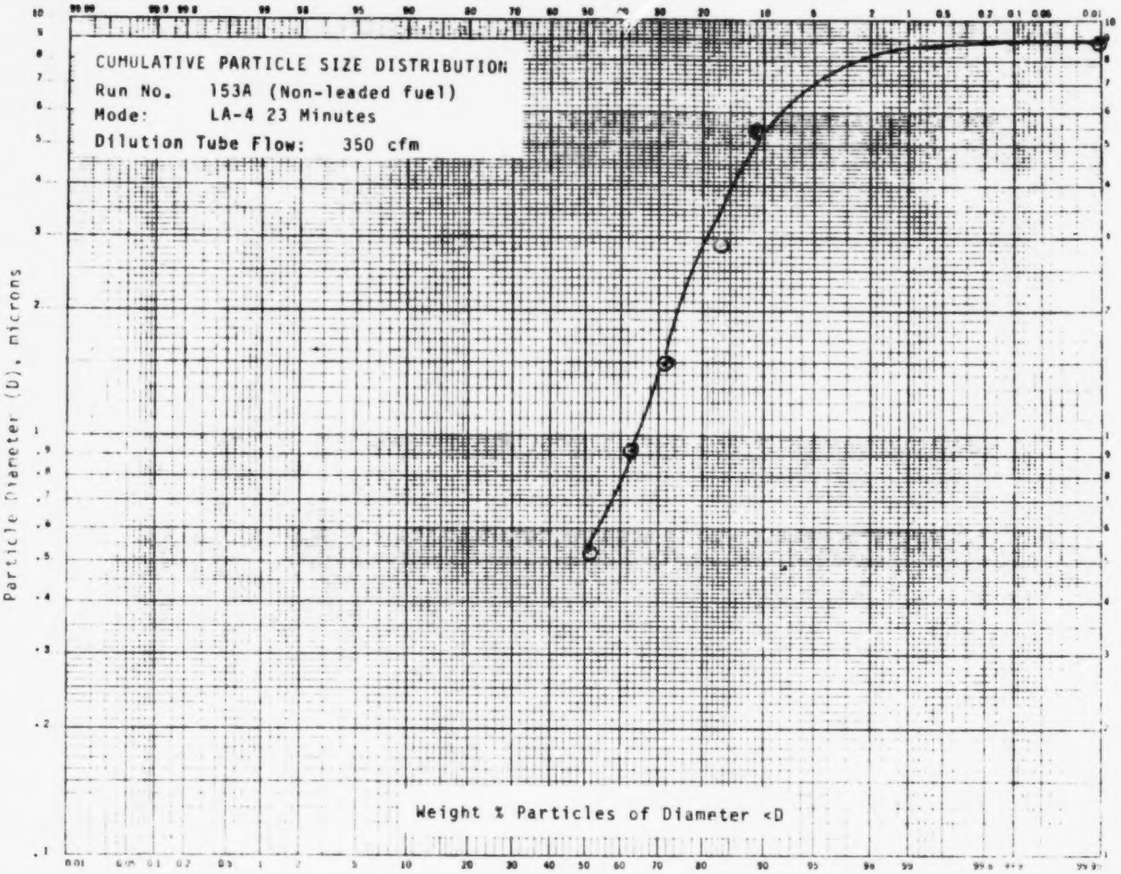

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 159A (Non-leaded fuel)
Mode: LA-4 41 Minutes
Dilution Tube Flow: 500 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99

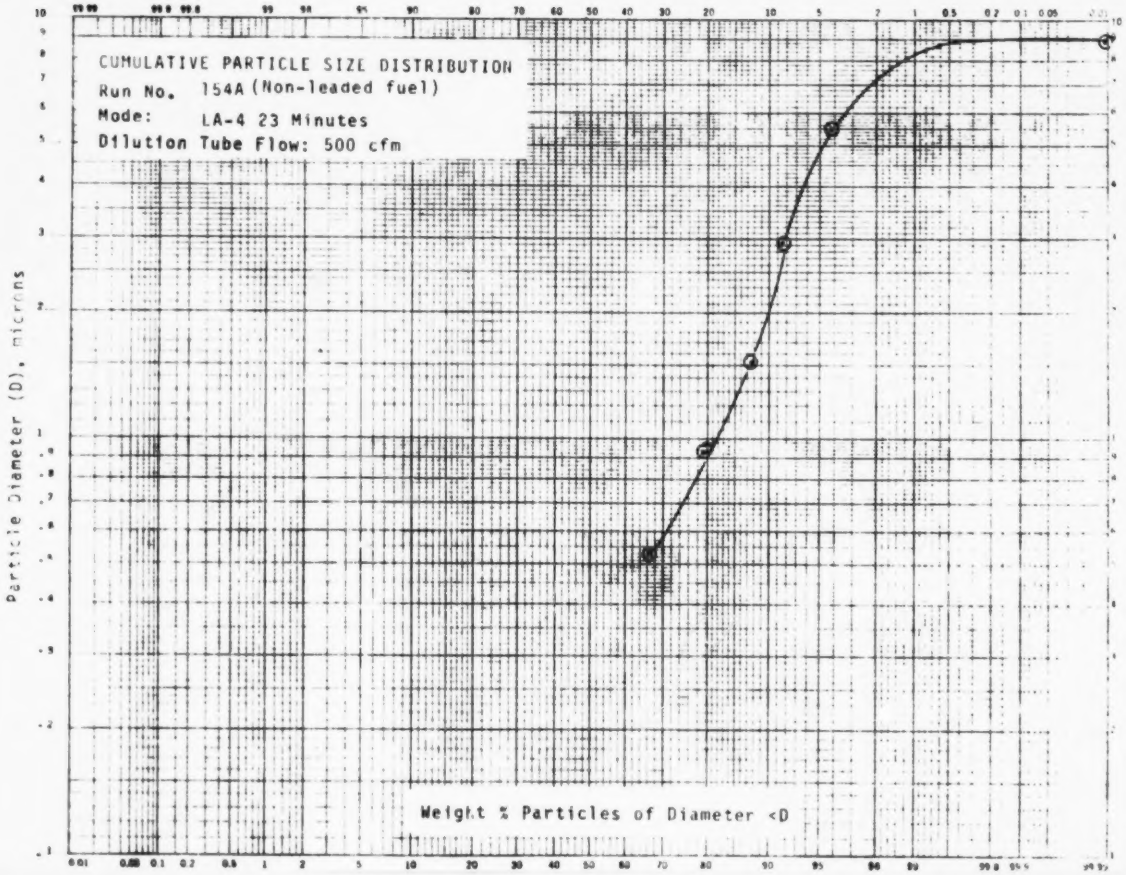

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 172A (Non-leaded fuel)
Mode: LA-4 41 Minutes
Dilution Tube Flow: 350 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D

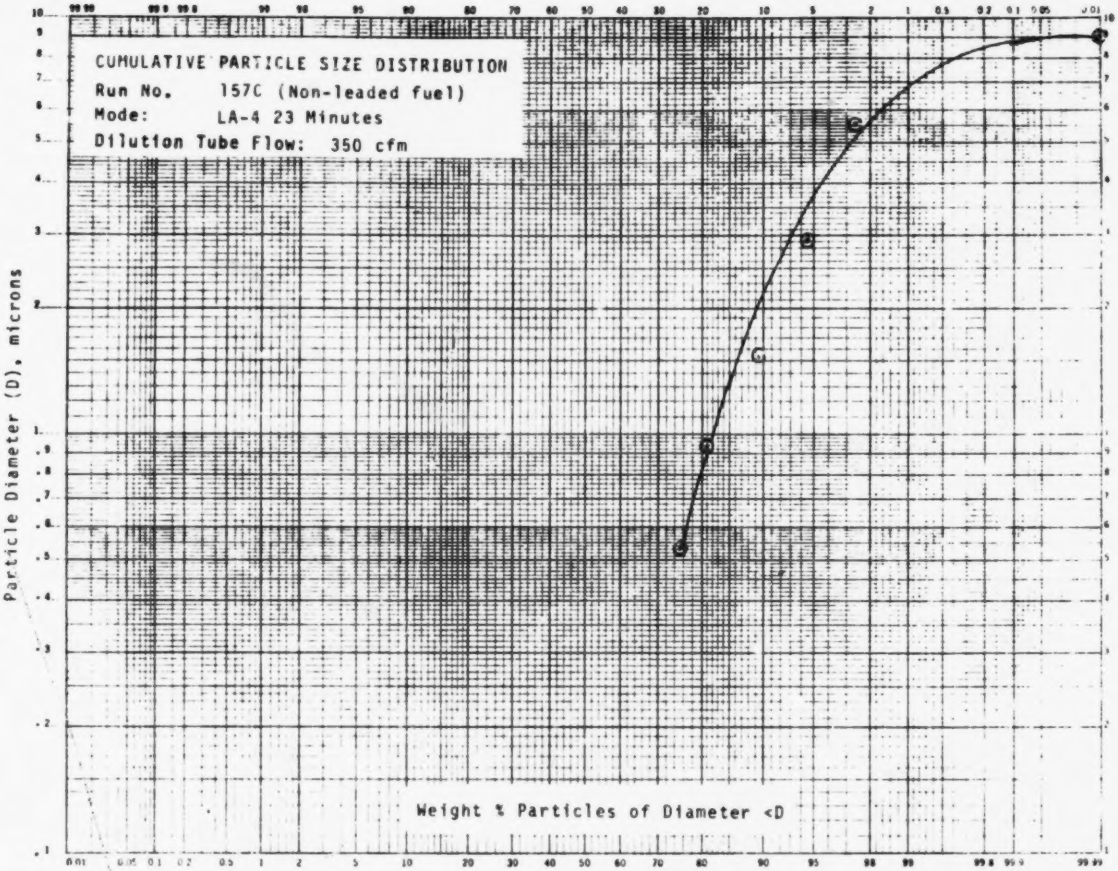

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 164C (Non-leaded fuel)
Mode: LA-4 23 Minutes
Dilution Tube Flow: 350 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D

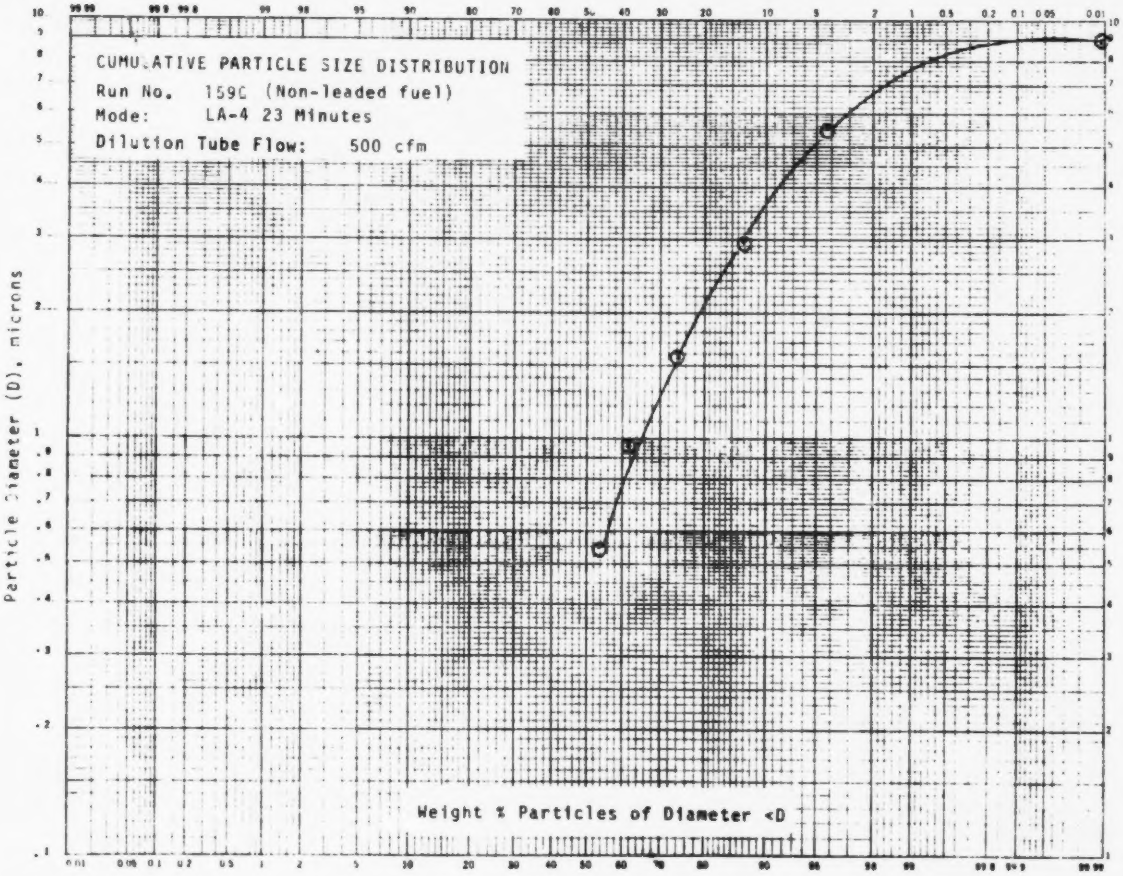

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 169C (Non-leaded fuel)
Mode: LA-4 23 Minutes
Dilution Tube Flow: 500 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.99
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.
2
3
4
5
6
7
8
9
10

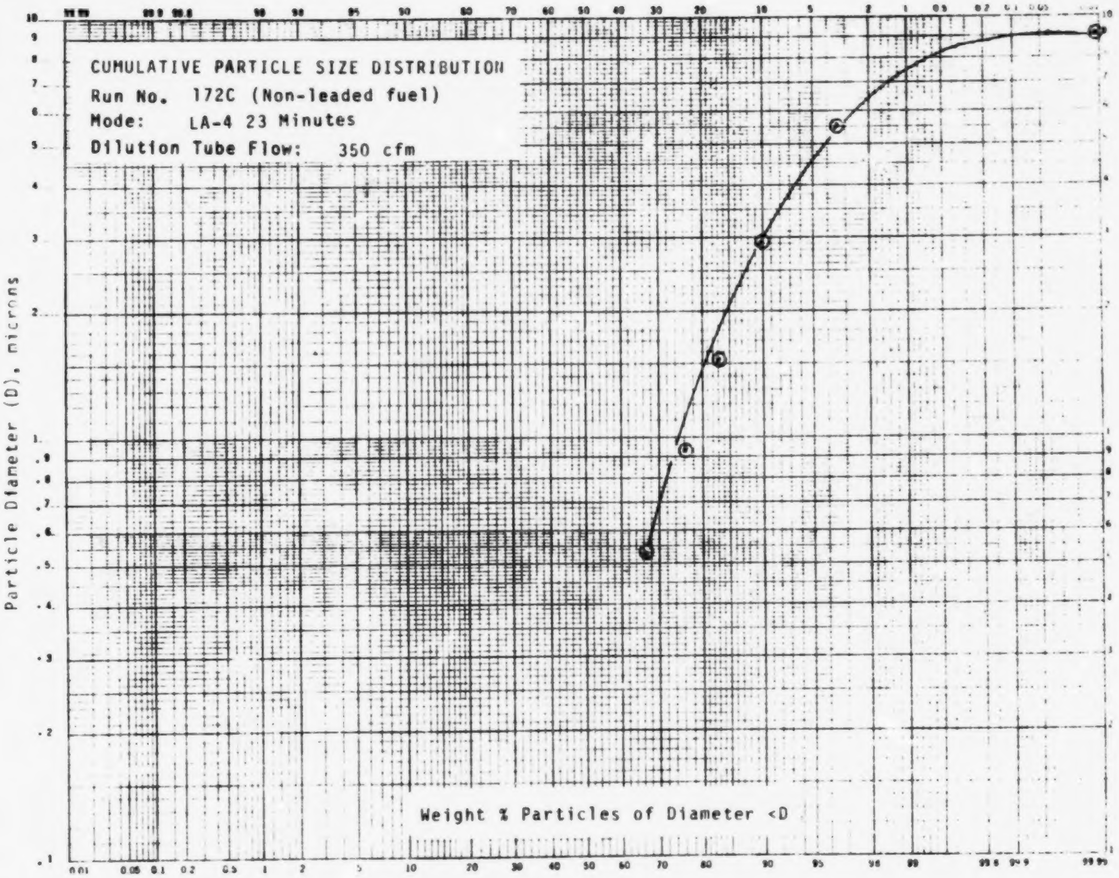

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 152A (Non-leaded fuel)
Mode: LA-4 23 Minutes
Dilution Tube Flow: 350 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.99
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.
2
3
4
5
6
7
8
9
10

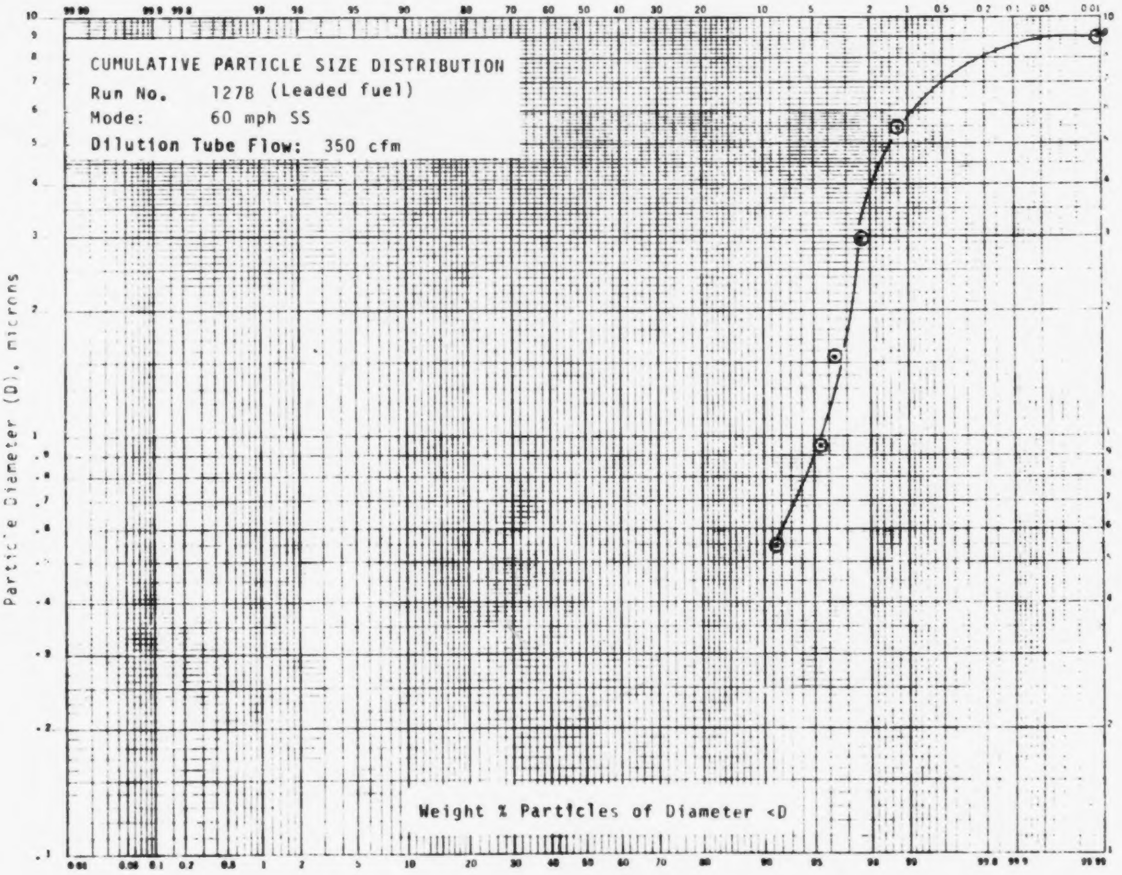

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 153A (Non-leaded fuel)
Mode: LA-4 23 Minutes
Dilution Tube Flow: 350 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D
10
1
.1
0.01
0.1
1
10
50
90
99
99.99

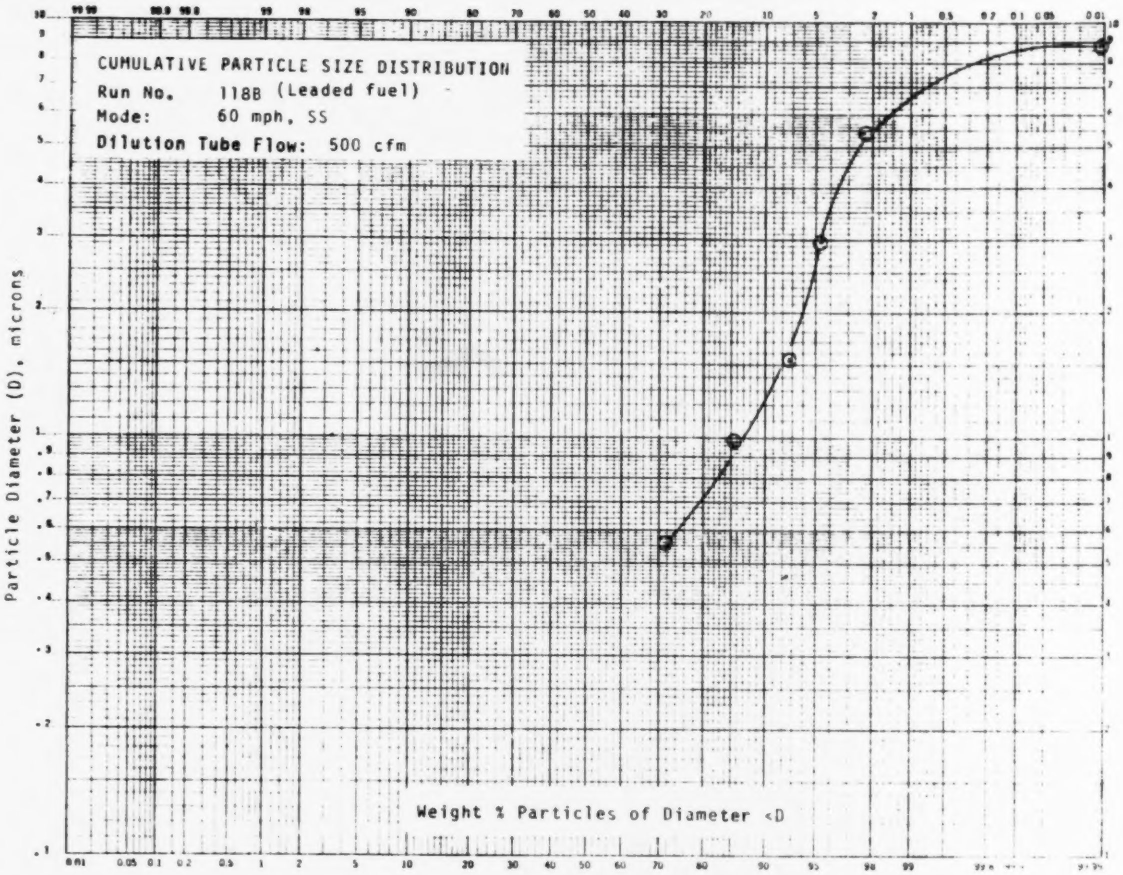

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 154A (Non-leaded fuel)
Mode: LA-4 23 Minutes
Dilution Tube Flow: 500 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D
10
1
.1
0.01
0.1
1
10
50
90
99
99.99


CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 157C (Non-leaded fuel)
Mode: LA-4 23 Minutes
Dilution Tube Flow: 350 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D


CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 159C (Non-leaded fuel)
Mode: LA-4 23 Minutes
Dilution Tube Flow: 500 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D


CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 172C (Non-leaded fuel)
Mode: LA-4 23 Minutes
Dilution Tube Flow: 350 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D


CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 127B (Leaded fuel)
Mode: 60 mph SS
Dilution Tube Flow: 350 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D


CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 118B (Leaded fuel)
Mode: 60 mph, SS
Dilution Tube Flow: 500 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
.1
.2
.3
.4
.5
.6
.7
.8
.9
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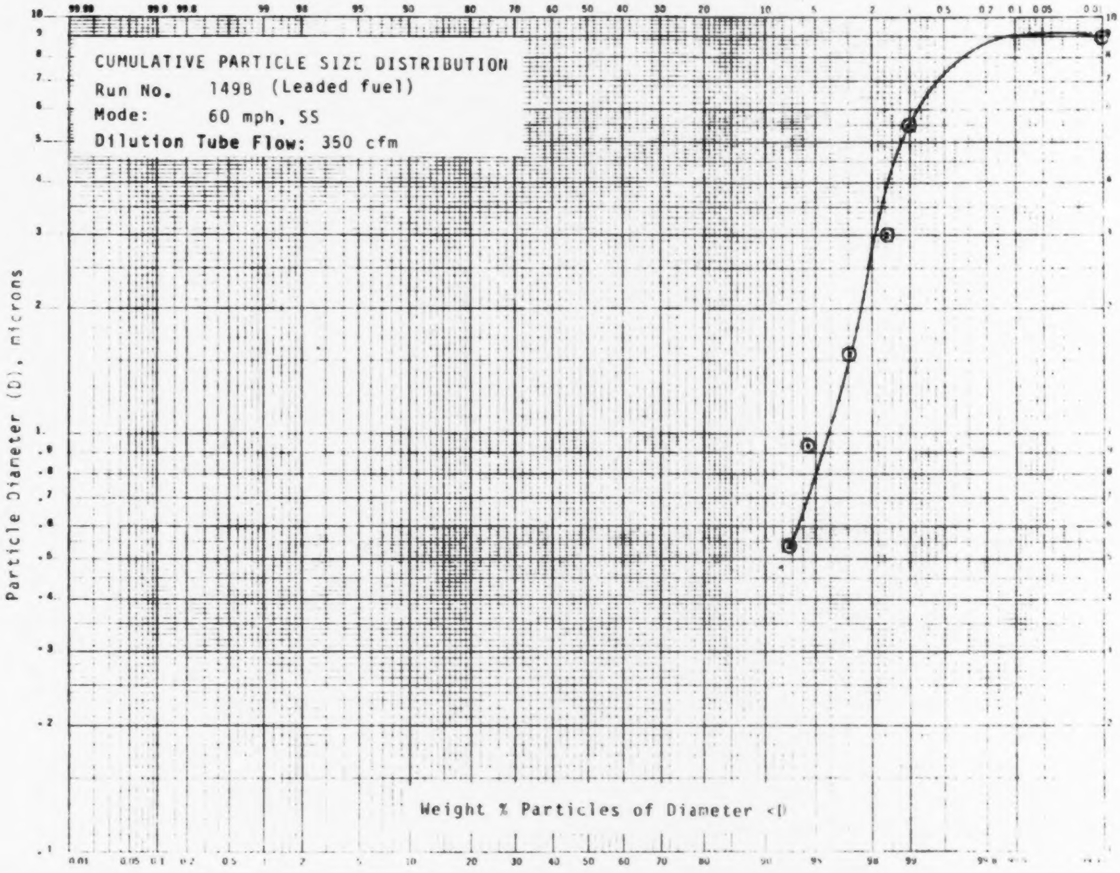
3
4
5
6
7
8
9
10


CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 149B (Leaded fuel)
Mode: 60 mph, SS
Dilution Tube Flow: 350 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
.1
.2
.3
.4
.5
.6
.7
.8
.9
1
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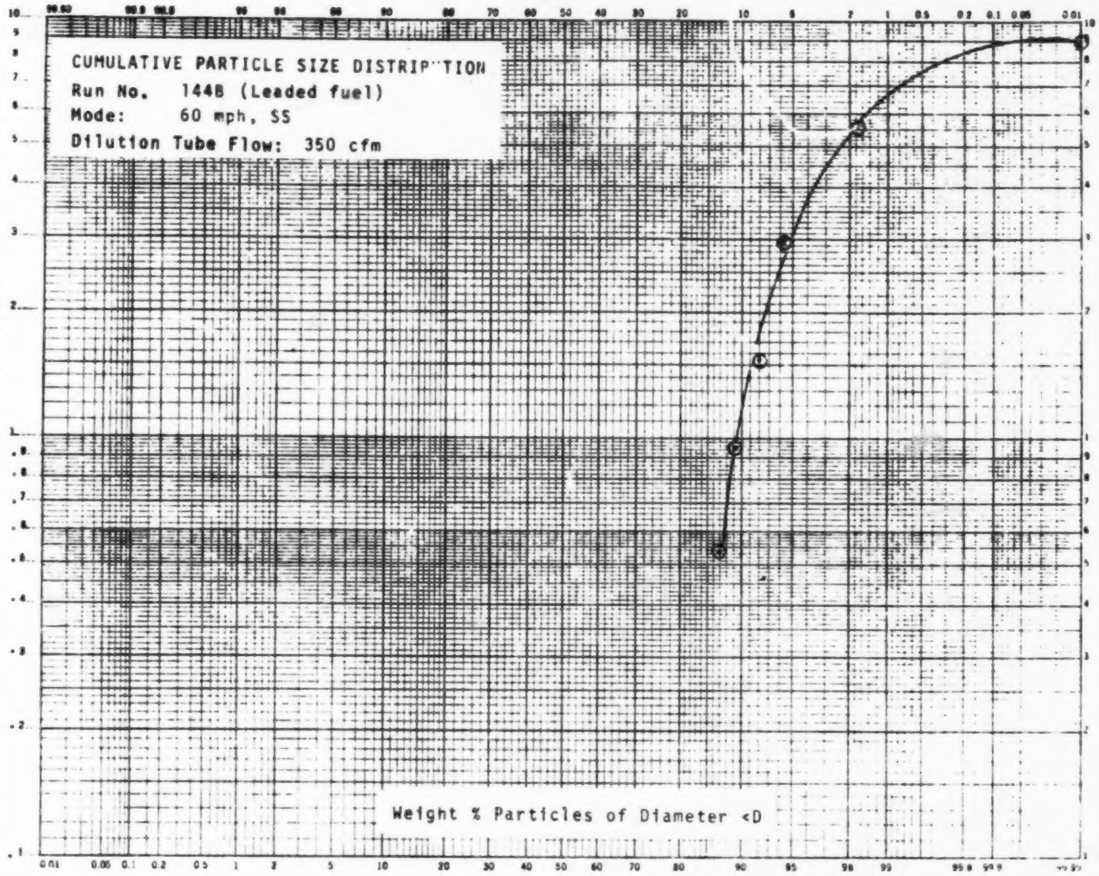
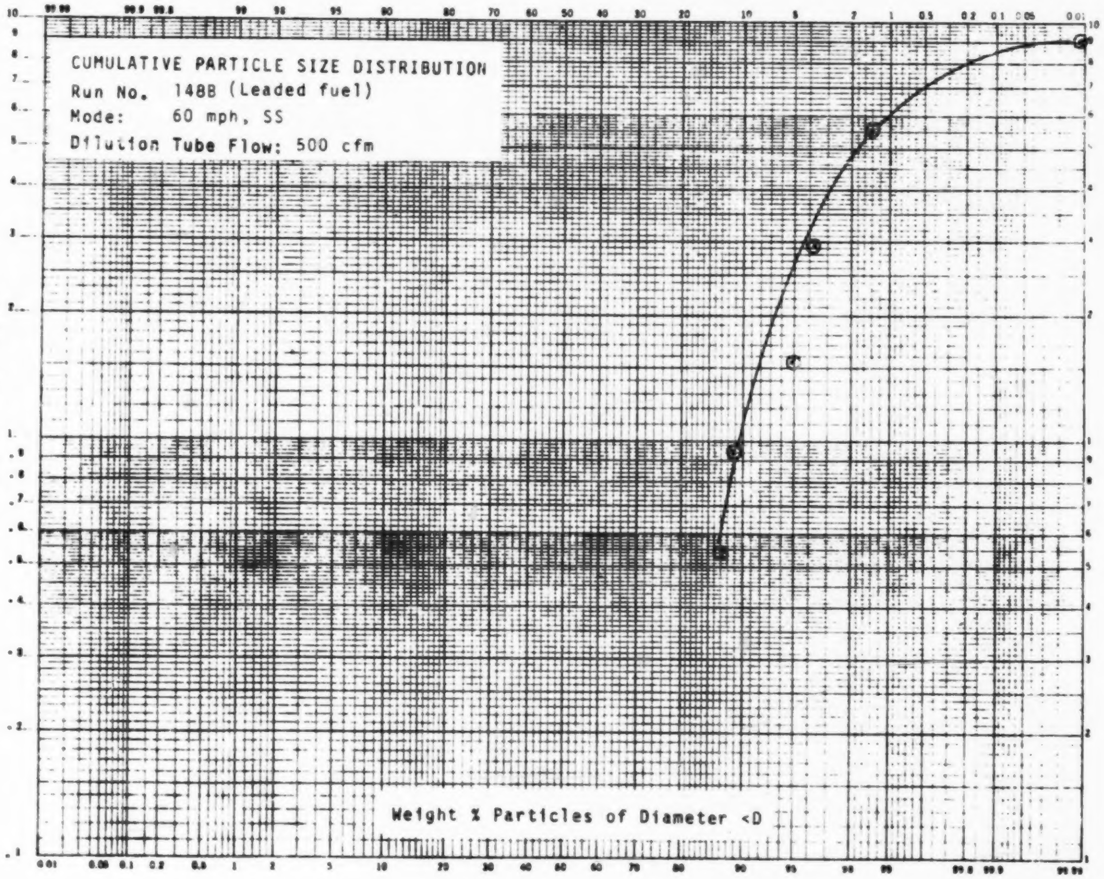
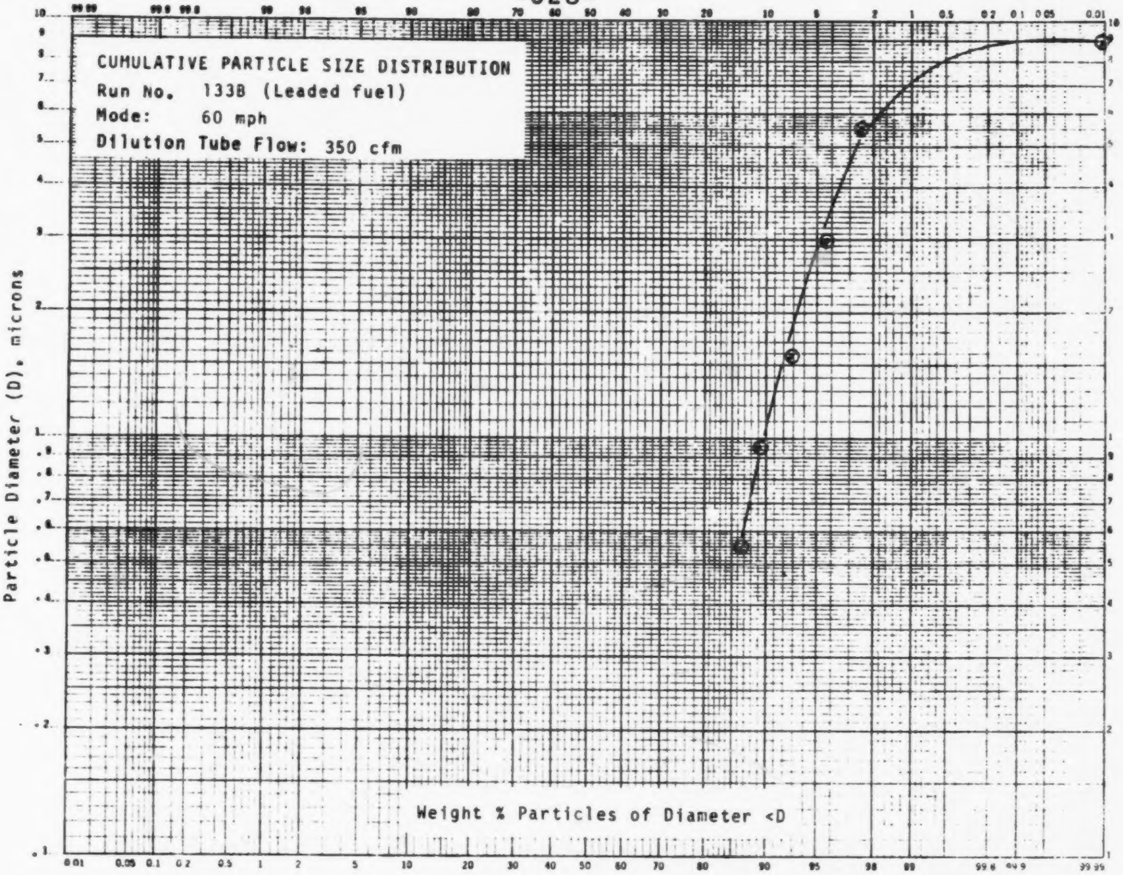
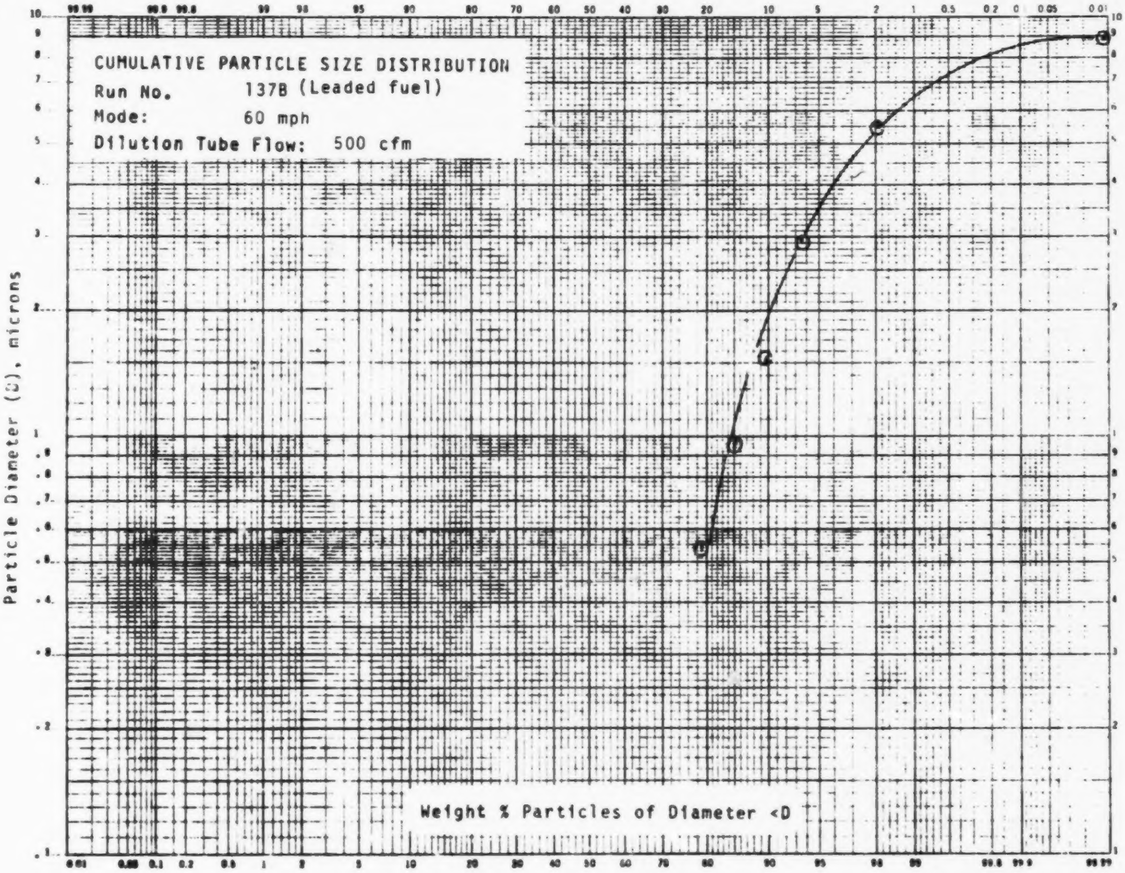
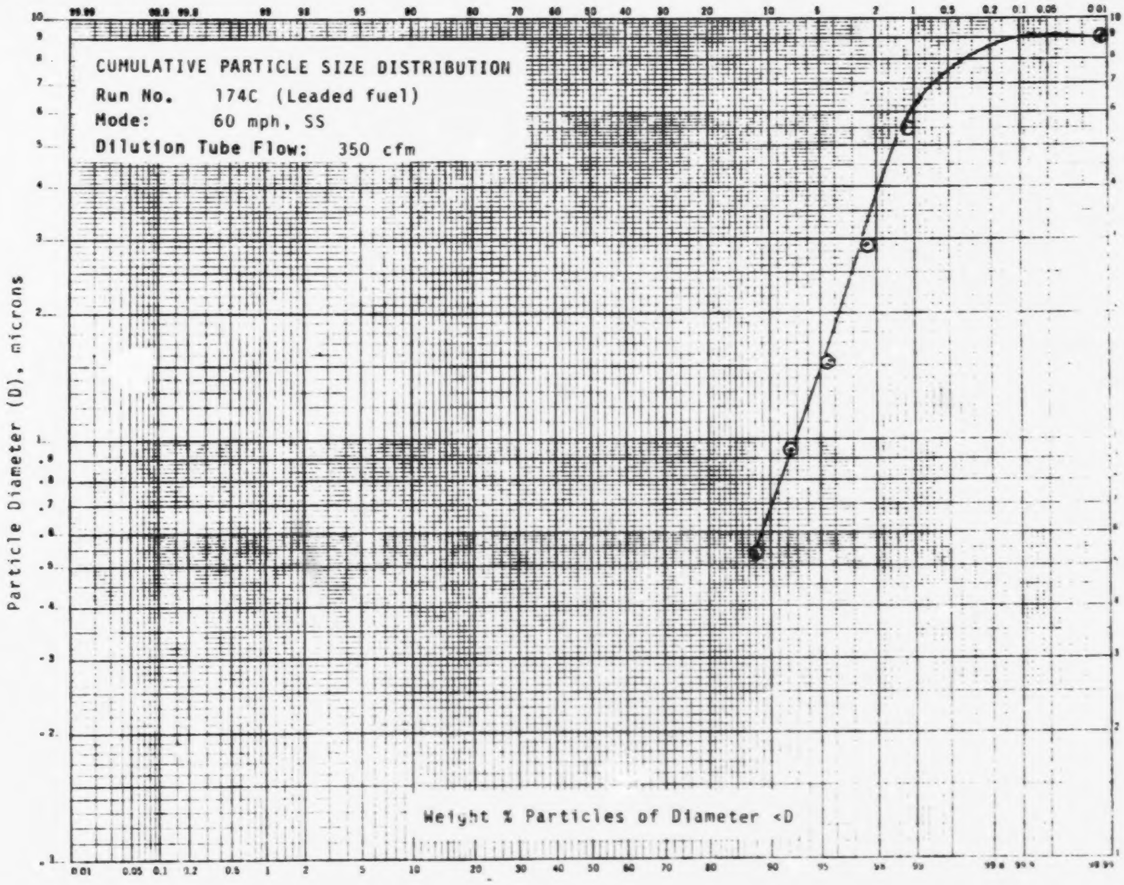
3
4
5
6
7
8
9
10

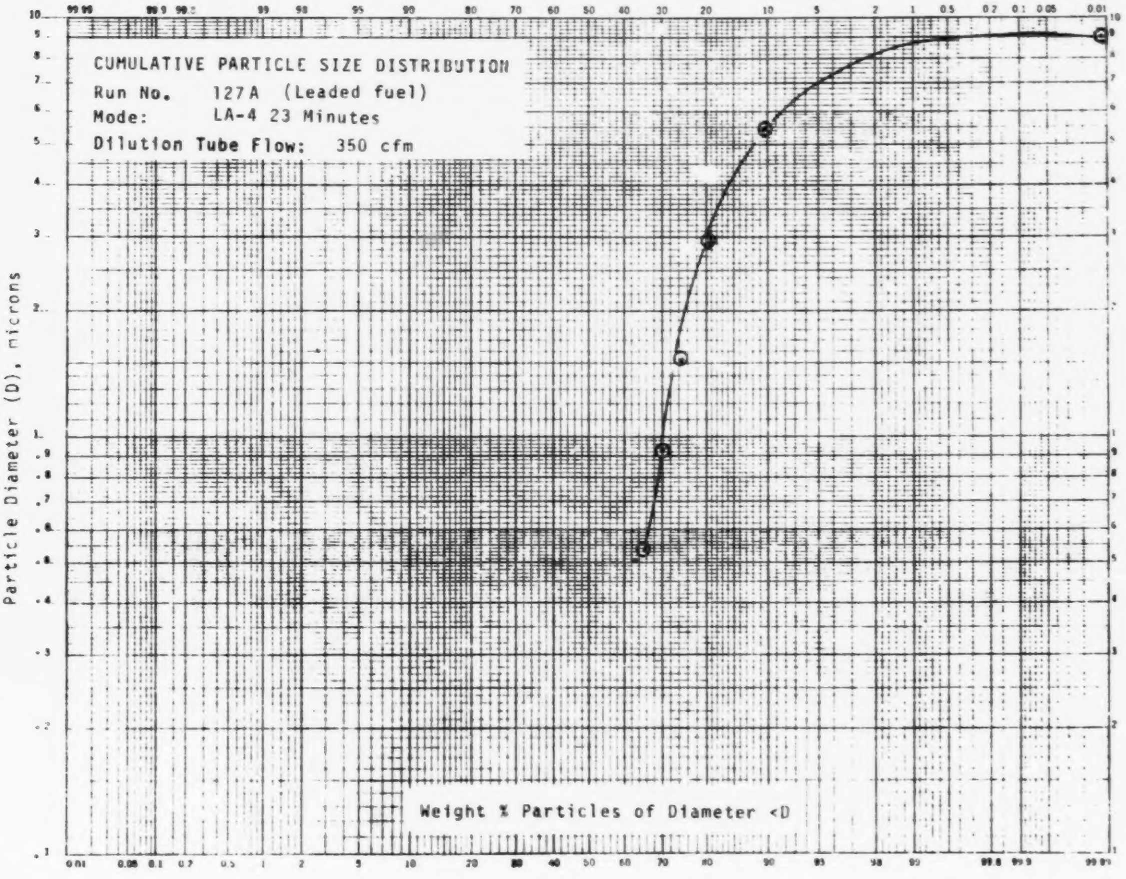

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 144B (Leaded fuel)
Mode: 60 mph, SS
Dilution Tube Flow: 350 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D

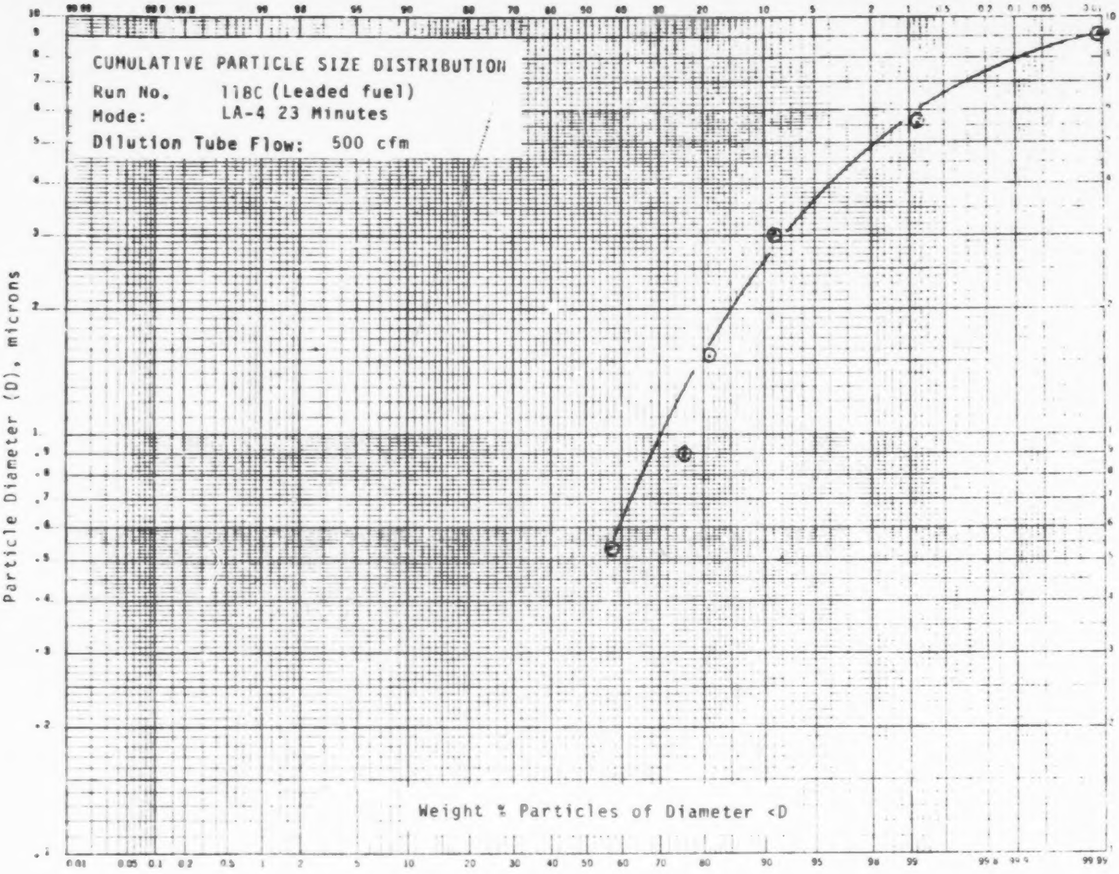

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 148B (Leaded fuel)
Mode: 60 mph, SS
Dilution Tube Flow: 500 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D

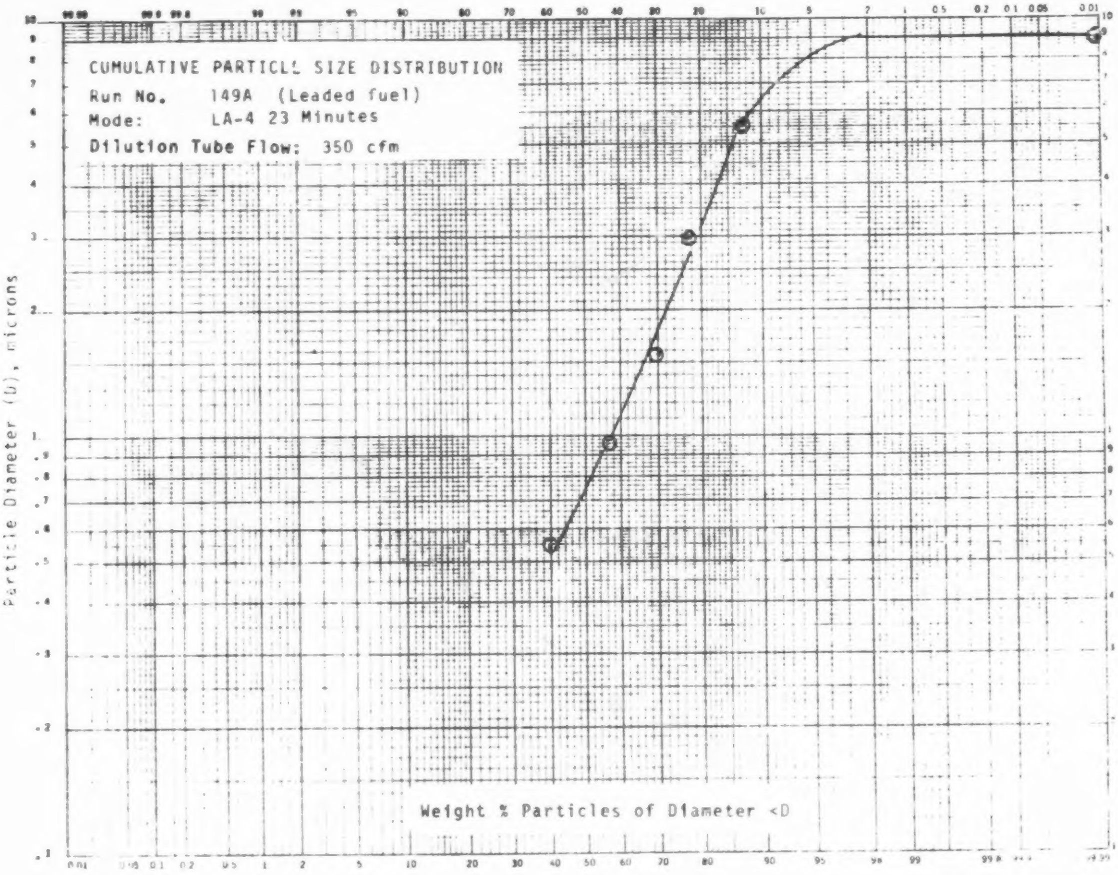

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 133B (Leaded fuel)
Mode: 60 mph
Dilution Tube Flow: 350 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99

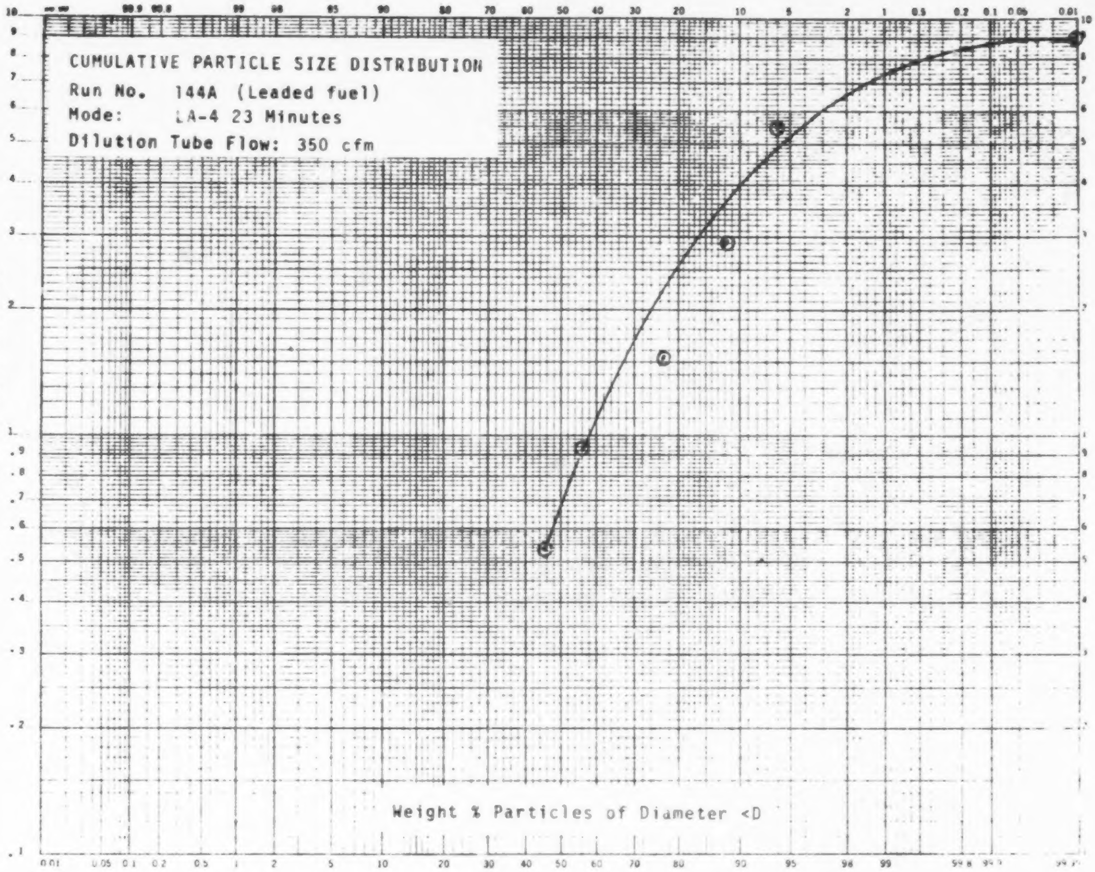

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 137B (Leaded fuel)
Mode: 60 mph
Dilution Tube Flow: 500 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99

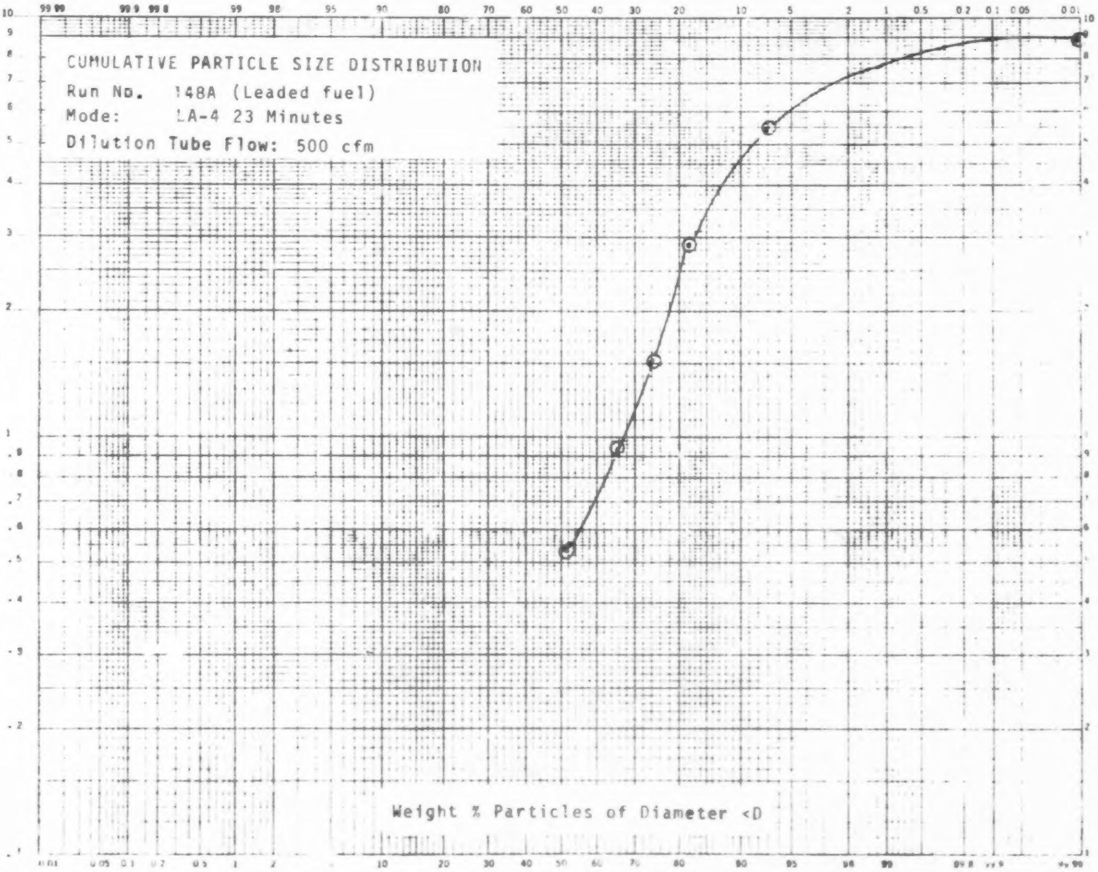

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 174C (Leaded fuel)
Mode: 60 mph, SS
Dilution Tube Flow: 350 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99

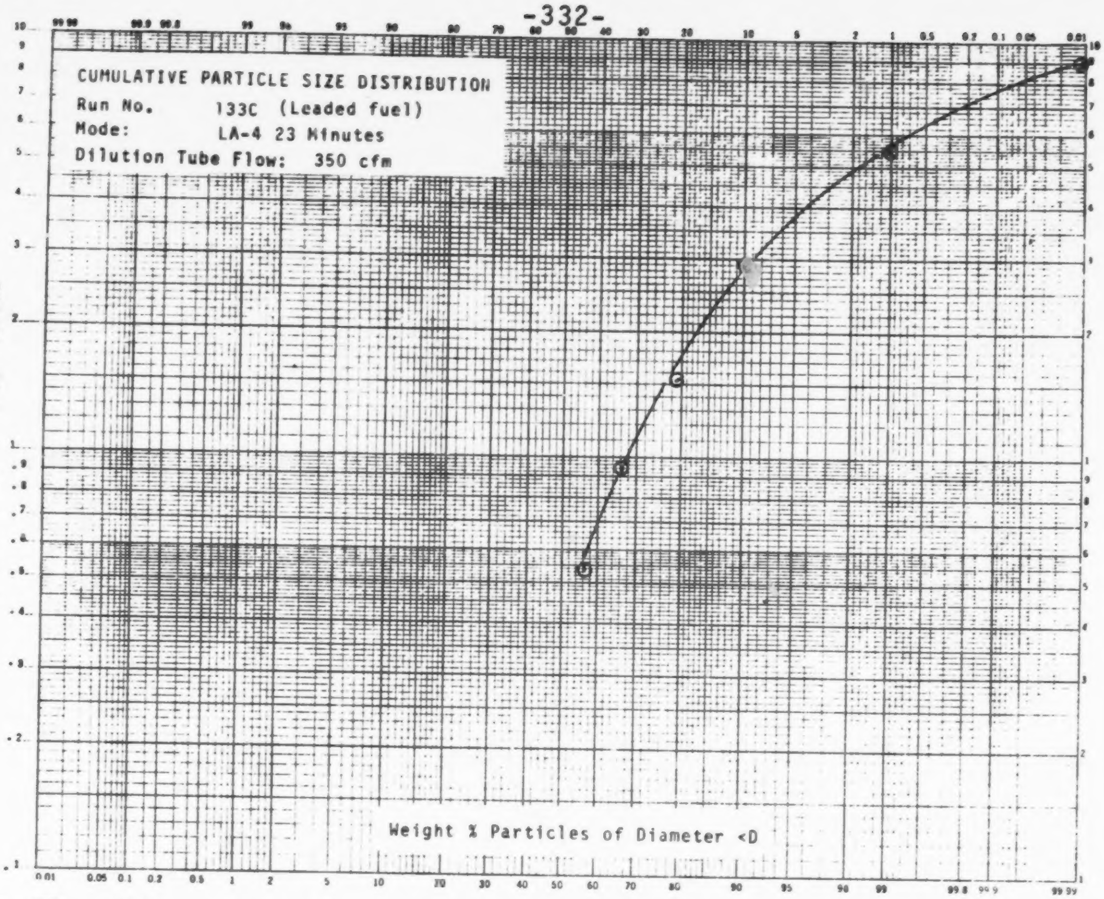

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 127A (Leaded fuel)
Mode: LA-4 23 Minutes
Dilution Tube Flow: 350 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99


CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 118C (Leaded fuel)
Mode: LA-4 23 Minutes
Dilution Tube Flow: 500 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D

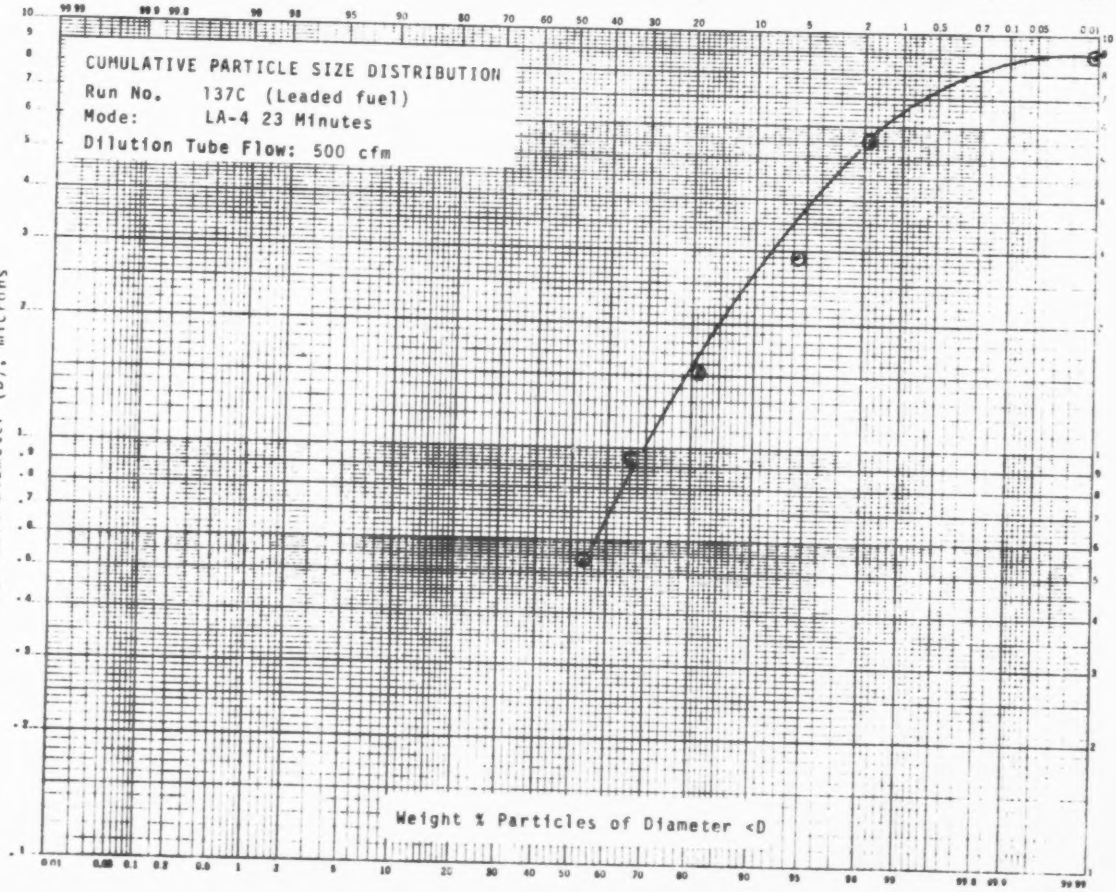

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 149A (Leaded fuel)
Mode: LA-4 23 Minutes
Dilution Tube Flow: 350 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D


CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 144A (Leaded fuel)
Mode: LA-4 23 Minutes
Dilution Tube Flow: 350 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D
99.99
99.9
99.8
99
98
95
90
80
70
60
50
40
30
20
10
5
2
1
0.5
0.2
0.1
0.05
0.01
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1

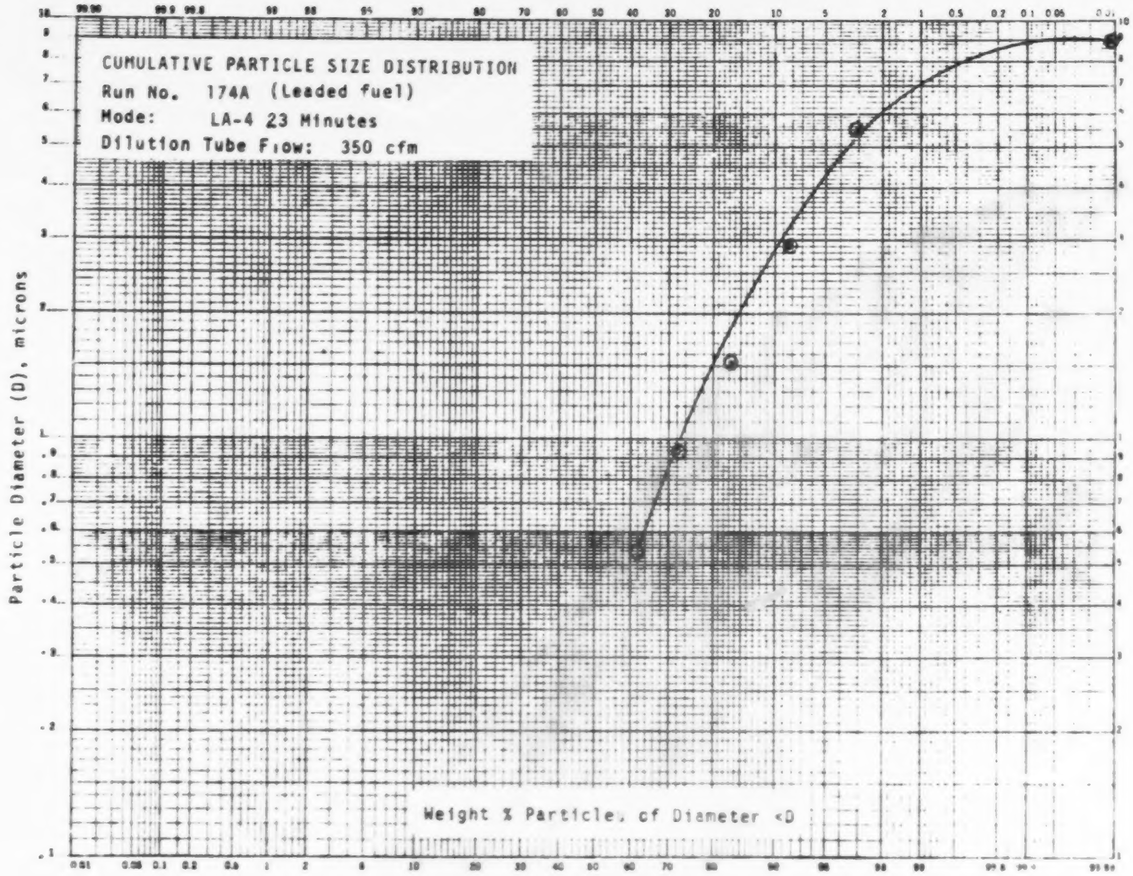

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 148A (Leaded fuel)
Mode: LA-4 23 Minutes
Dilution Tube Flow: 500 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D
99.99
99.9
99.8
99
98
95
90
80
70
60
50
40
30
20
10
5
2
1
0.5
0.2
0.1
0.05
0.01
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1

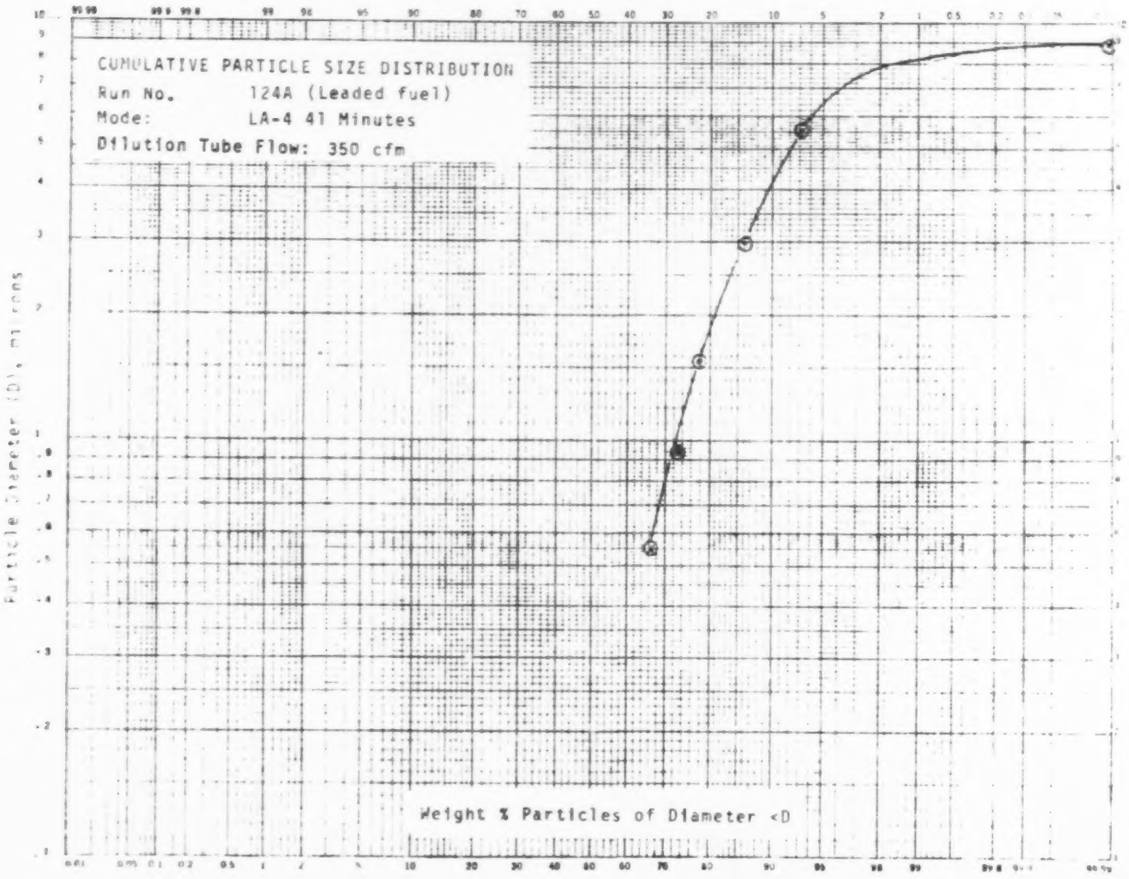


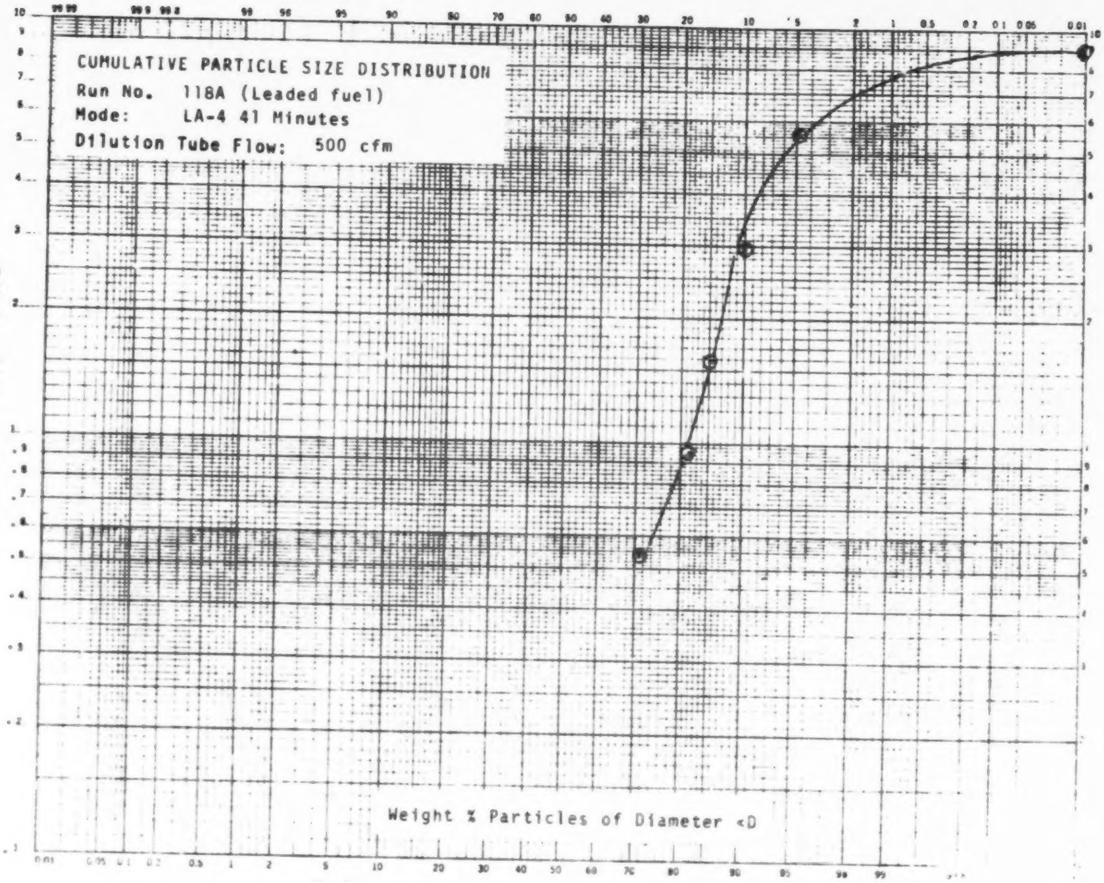
CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 133C (Leaded fuel)
Mode: LA-4 23 Minutes
Dilution Tube Flow: 350 cfm

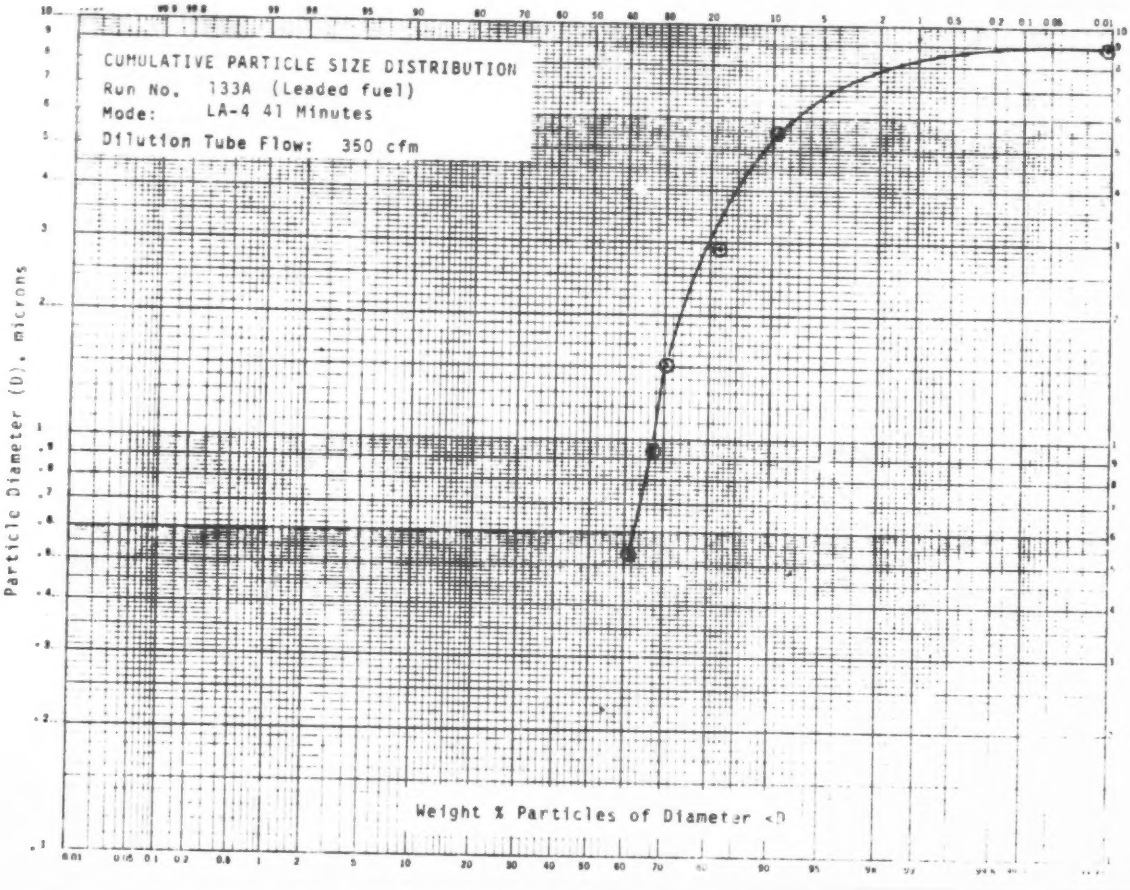


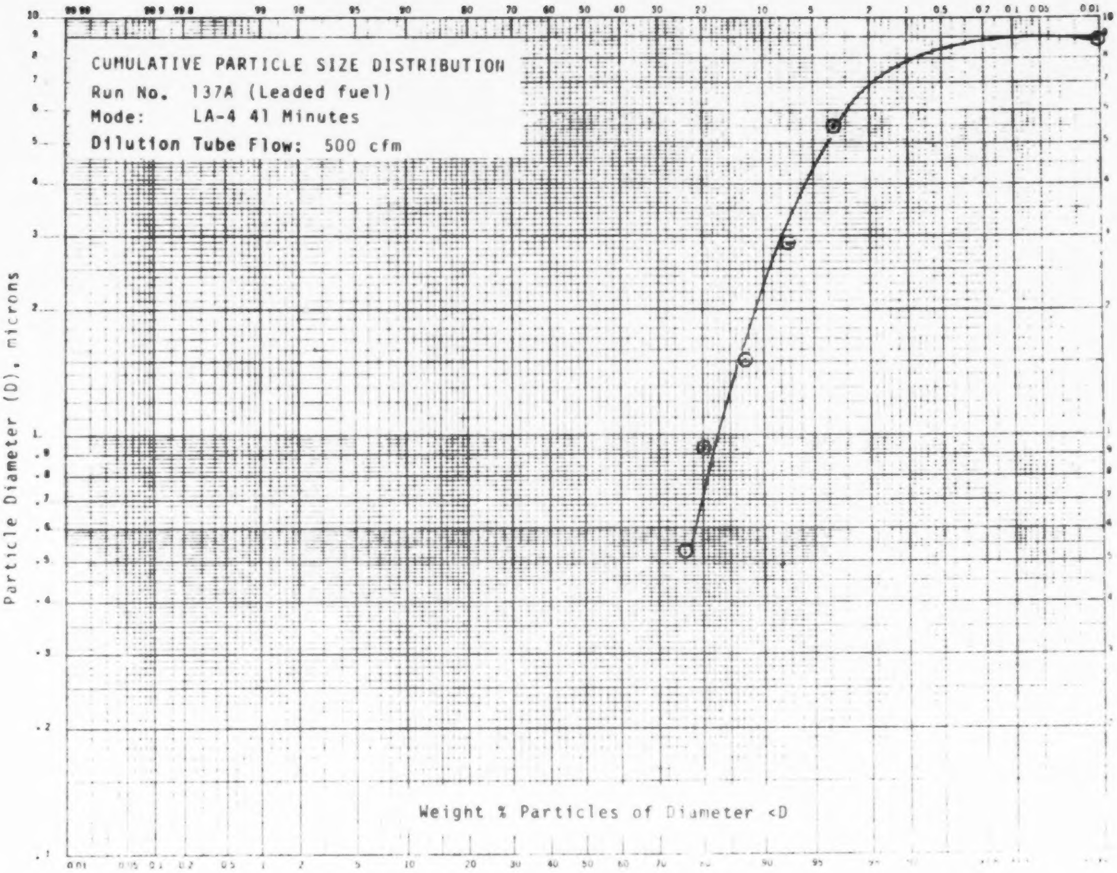
CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 137C (Leaded fuel)
Mode: LA-4 23 Minutes
Dilution Tube Flow: 500 cfm

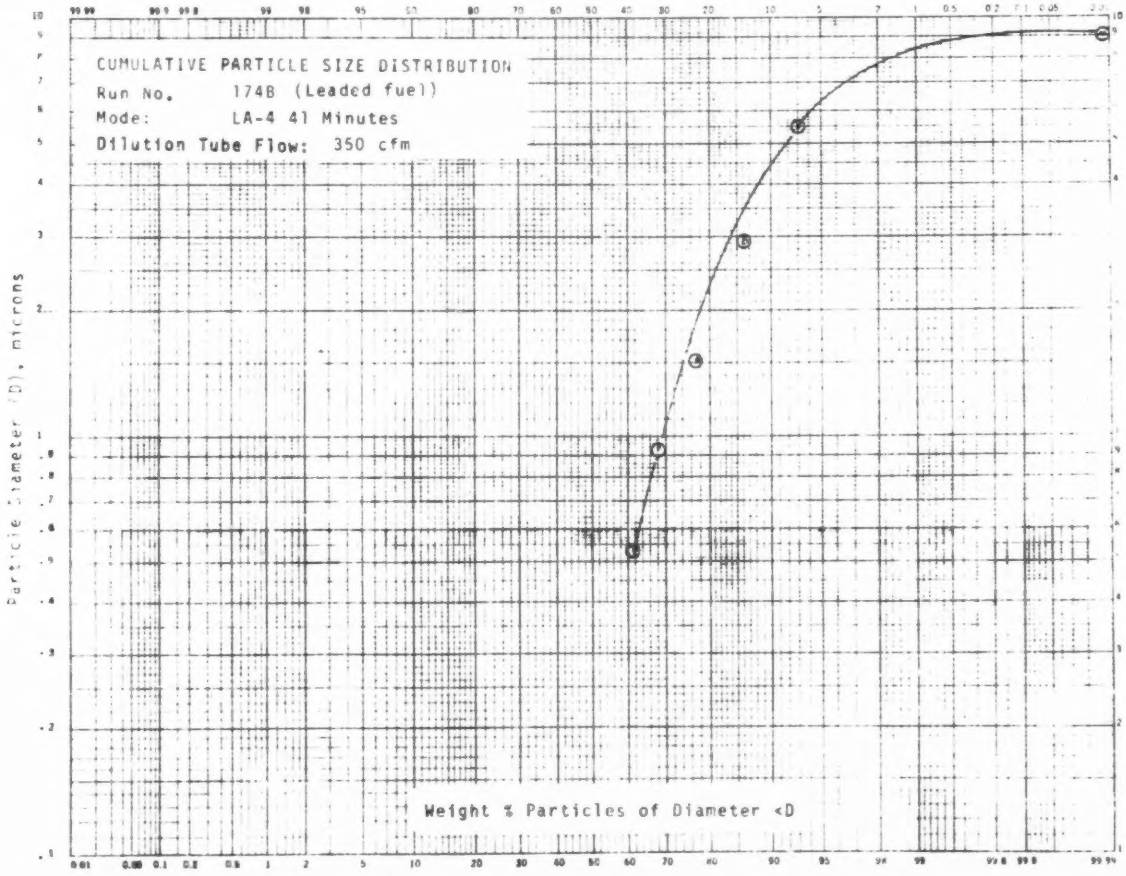

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 174A (Leaded fuel)
Mode: LA-4 23 Minutes
Dilution Tube Flow: 350 cfm

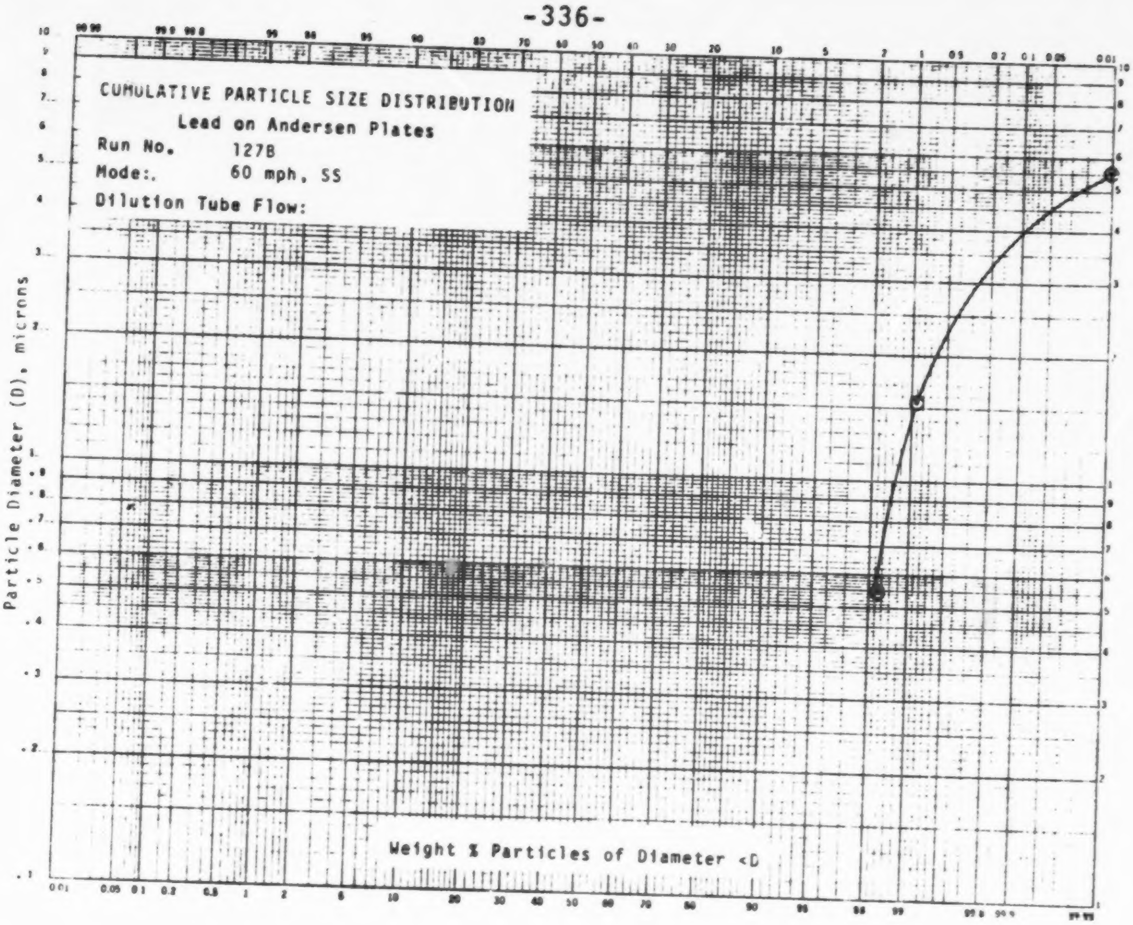

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 124A (Leaded fuel)
Mode: LA-4 41 Minutes
Dilution Tube Flow: 350 cfm

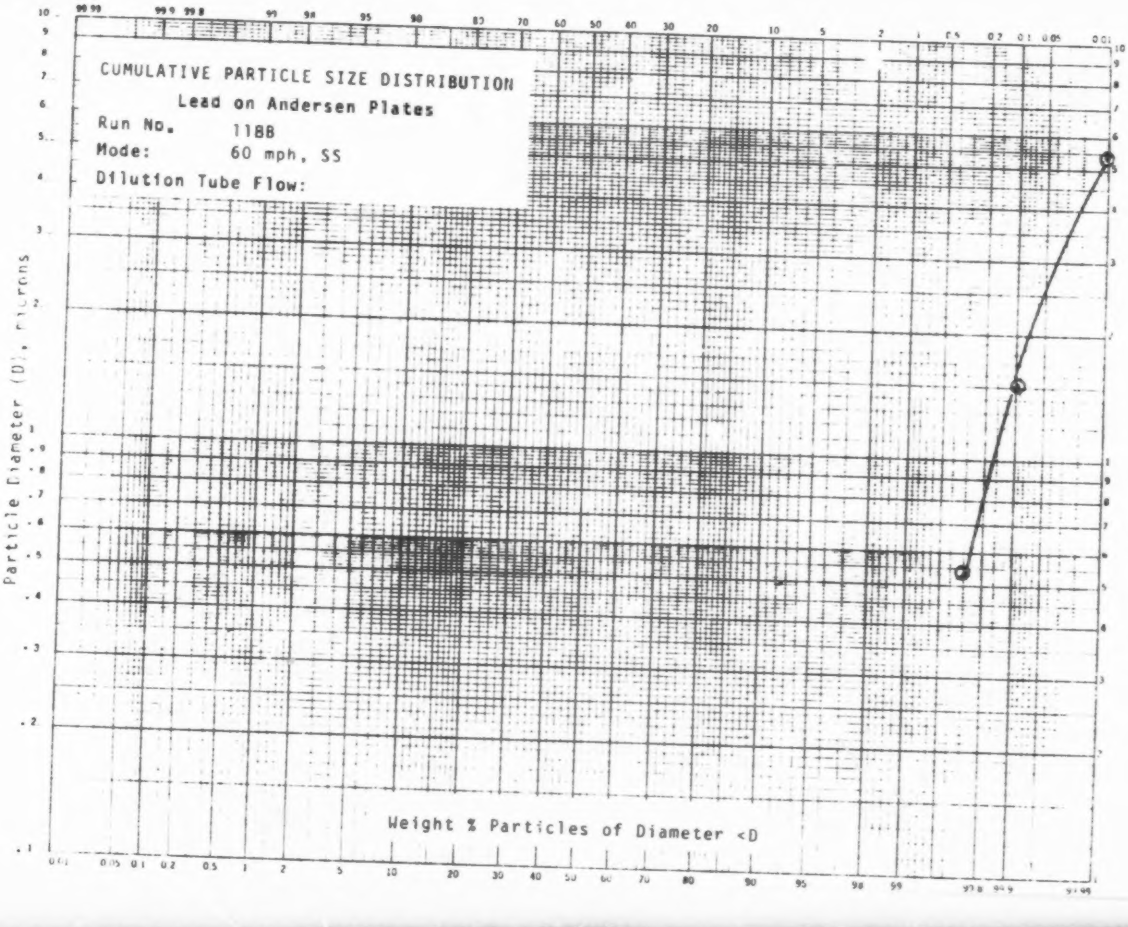

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 118A (Leaded fuel)
Mode: LA-4 41 Minutes
Dilution Tube Flow: 500 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D
10
.1
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.99
99.9
99.8

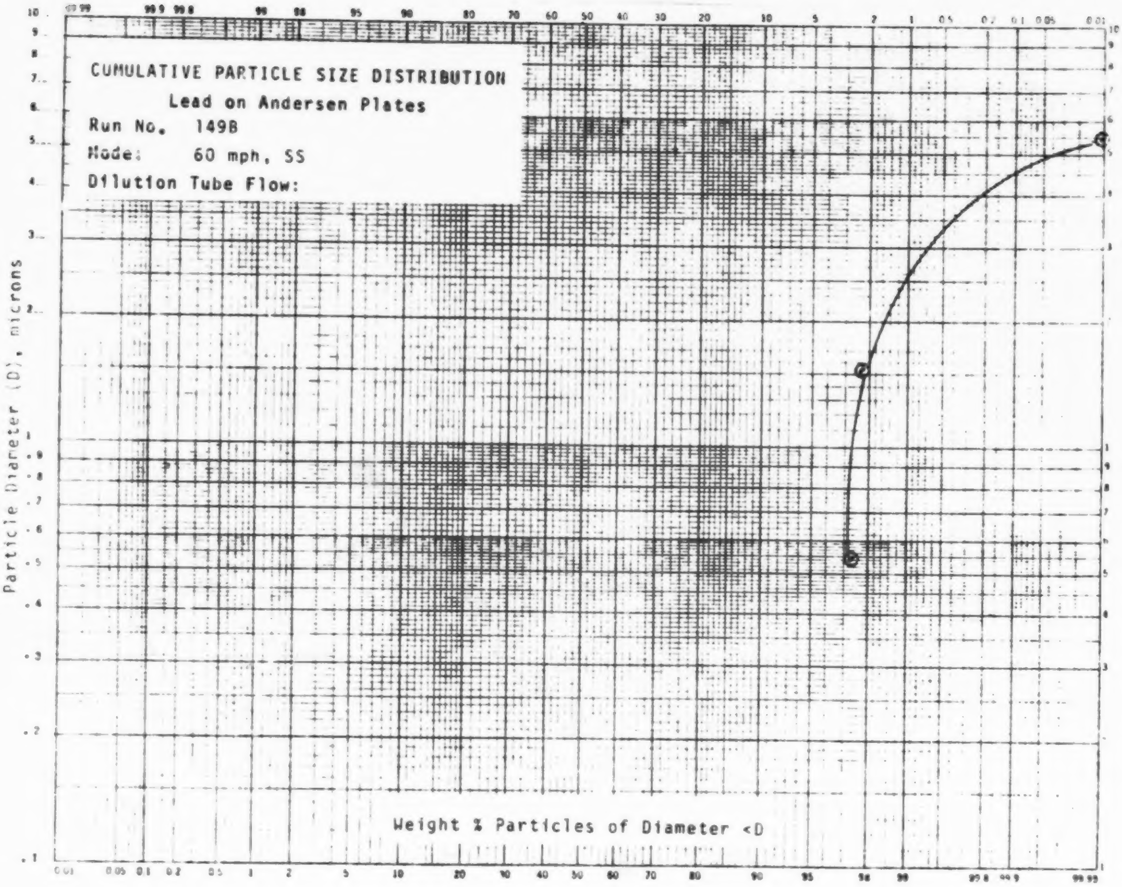

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 133A (Leaded fuel)
Mode: LA-4 41 Minutes
Dilution Tube Flow: 350 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D
10
.1
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.9
99.8


CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 137A (Leaded fuel)
Mode: LA-4 41 Minutes
Dilution Tube Flow: 500 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D
99.99
99.9
99.8
99
98
95
90
80
70
60
50
40
30
20
10
5
2
1
0.5
0.2
0.1
0.05
0.01
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
10
1
.1

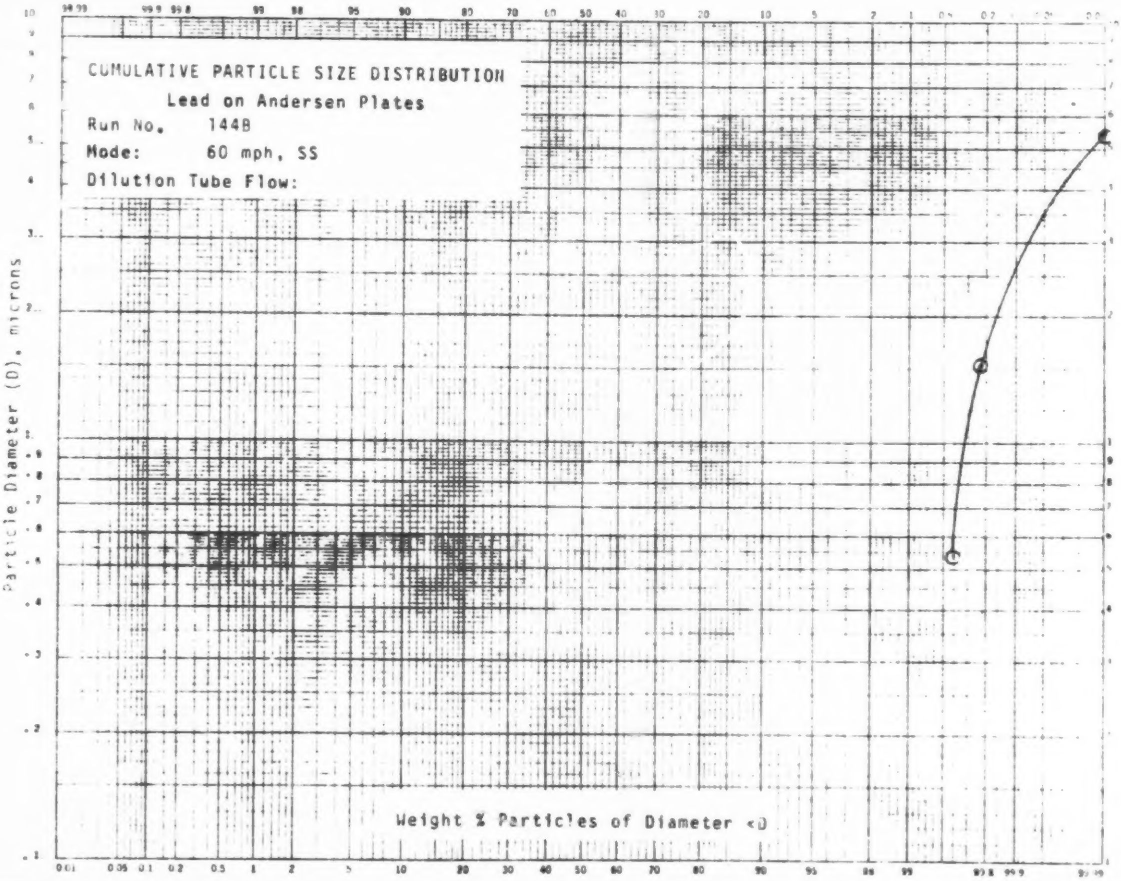

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Run No. 174B (Leaded fuel)
Mode: LA-4 41 Minutes
Dilution Tube Flow: 350 cfm
Particle Diameter (D), microns
Weight % Particles of Diameter <D
99.99
99.9
99.8
99
98
95
90
80
70
60
50
40
30
20
10
5
2
1
0.5
0.2
0.1
0.05
0.01
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99
10
1
.1


CUMULATIVE PARTICLE SIZE DISTRIBUTION
Lead on Andersen Plates
Run No. 127B
Mode: 60 mph, SS
Dilution Tube Flow:
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99

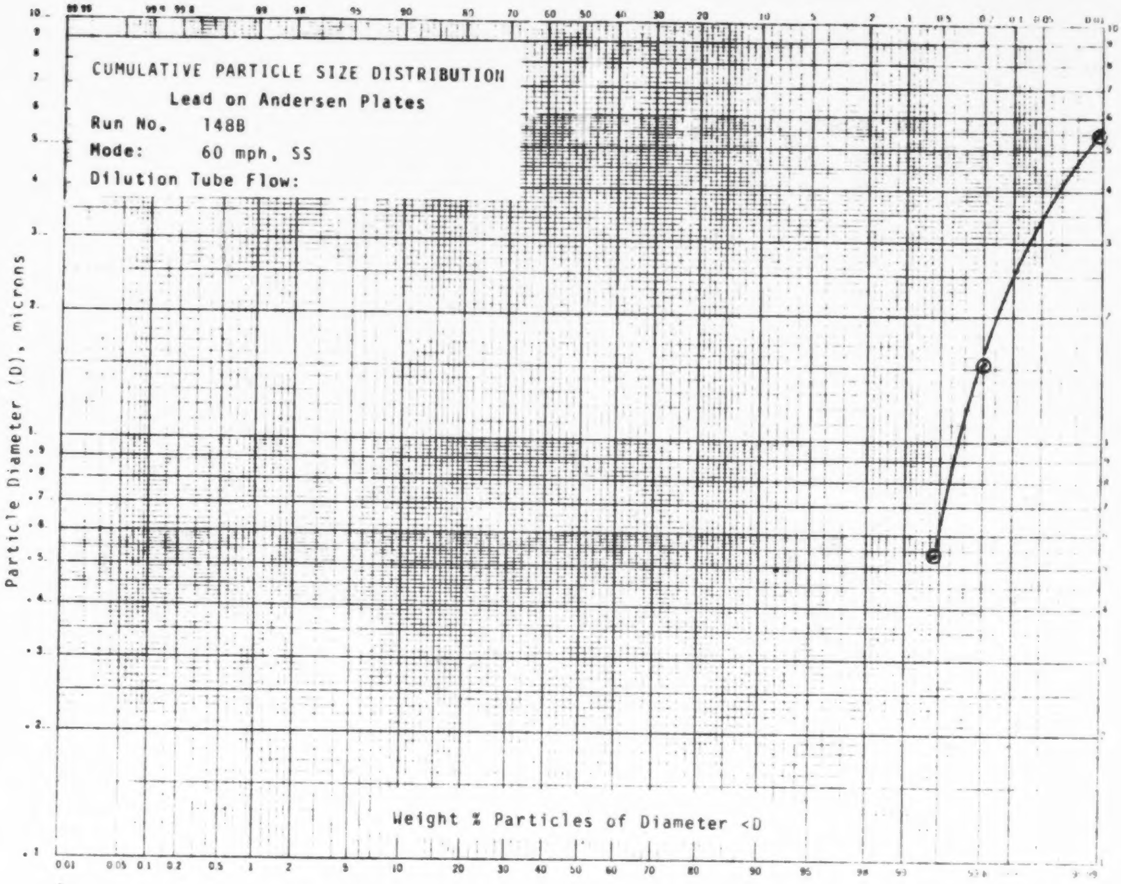

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Lead on Andersen Plates
Run No. 118B
Mode: 60 mph, SS
Dilution Tube Flow:
Particle Diameter (D), microns
Weight % Particles of Diameter <D
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99

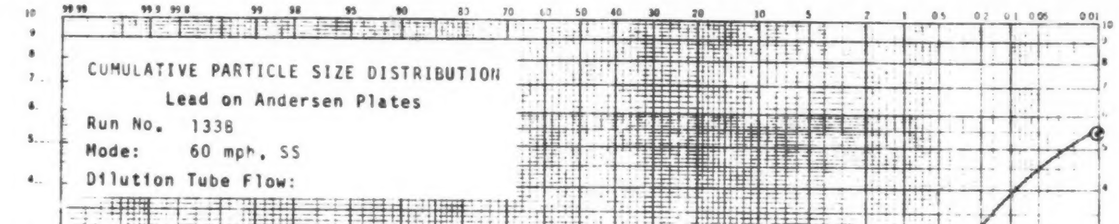


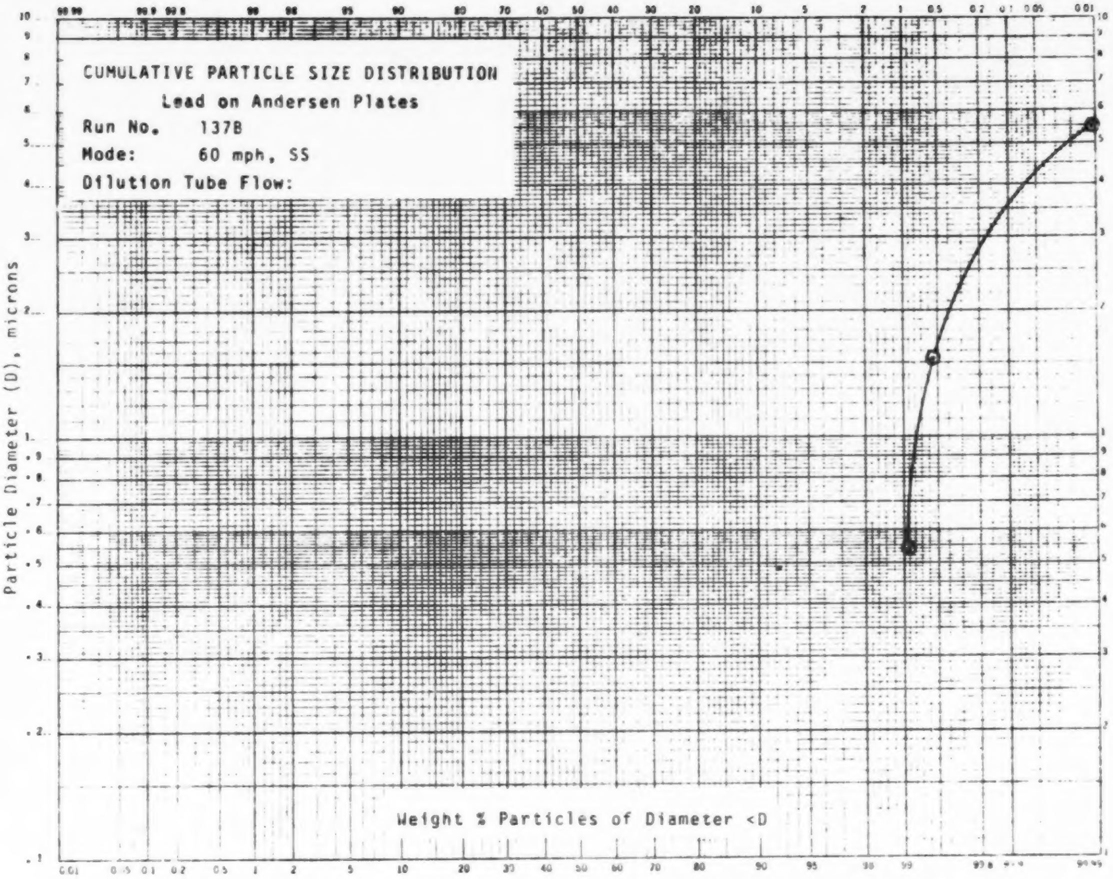
CUMULATIVE PARTICLE SIZE DISTRIBUTION
Lead on Andersen Plates
Run No. 149B
Mode: 60 mph, SS
Dilution Tube Flow:

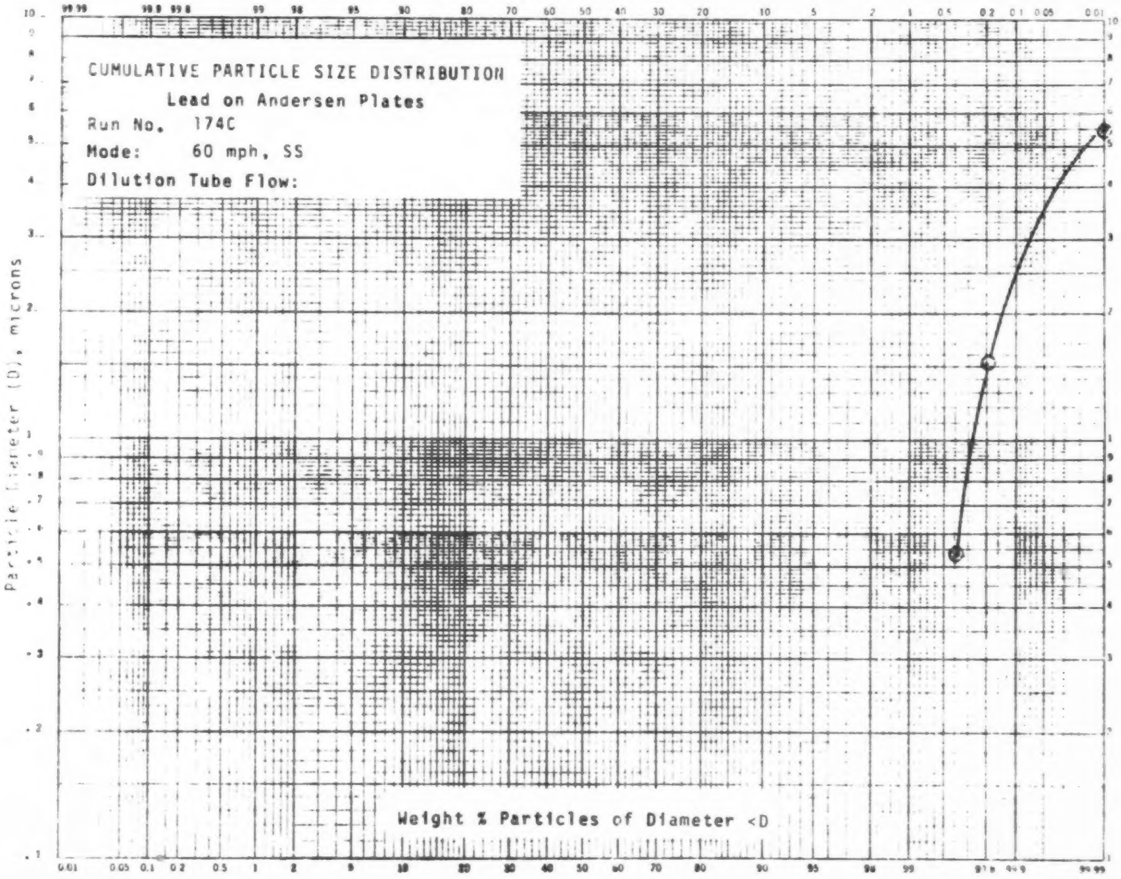


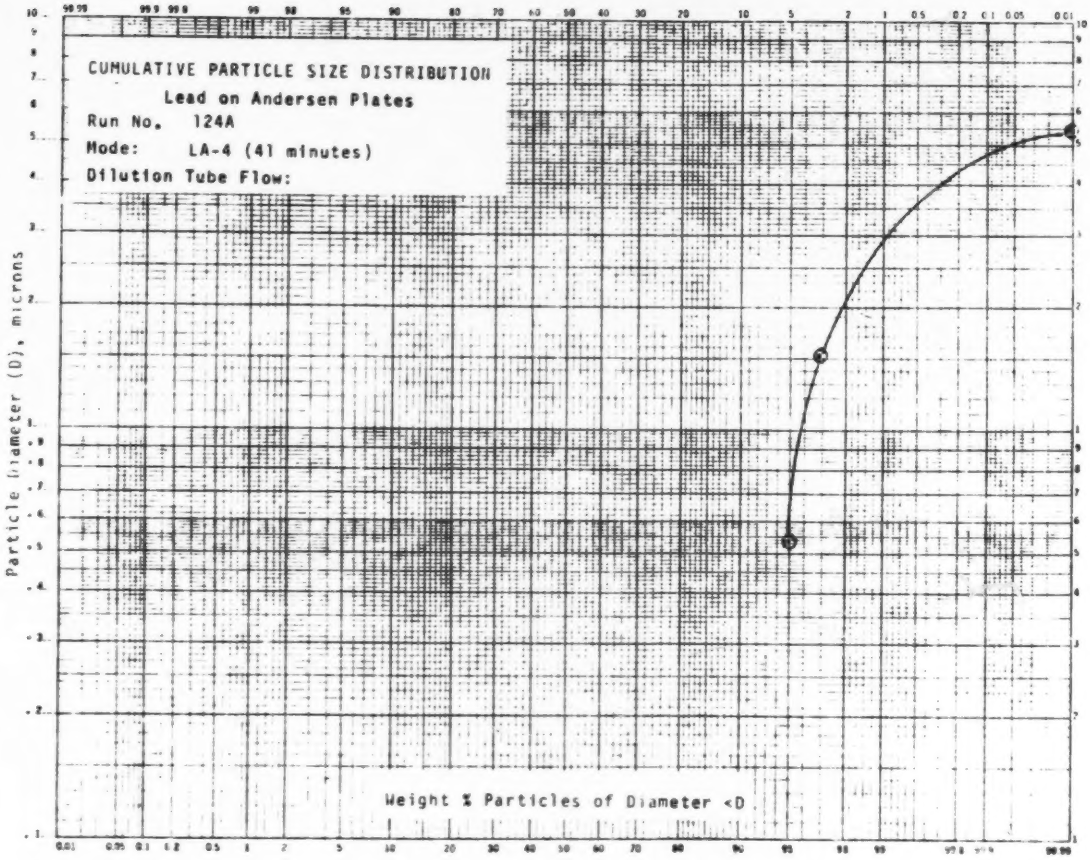
CUMULATIVE PARTICLE SIZE DISTRIBUTION
Lead on Andersen Plates
Run No. 144B
Mode: 60 mph, SS
Dilution Tube Flow:


CUMULATIVE PARTICLE SIZE DISTRIBUTION
Lead on Andersen Plates
Run No. 148B
Mode: 60 mph, SS
Dilution Tube Flow:

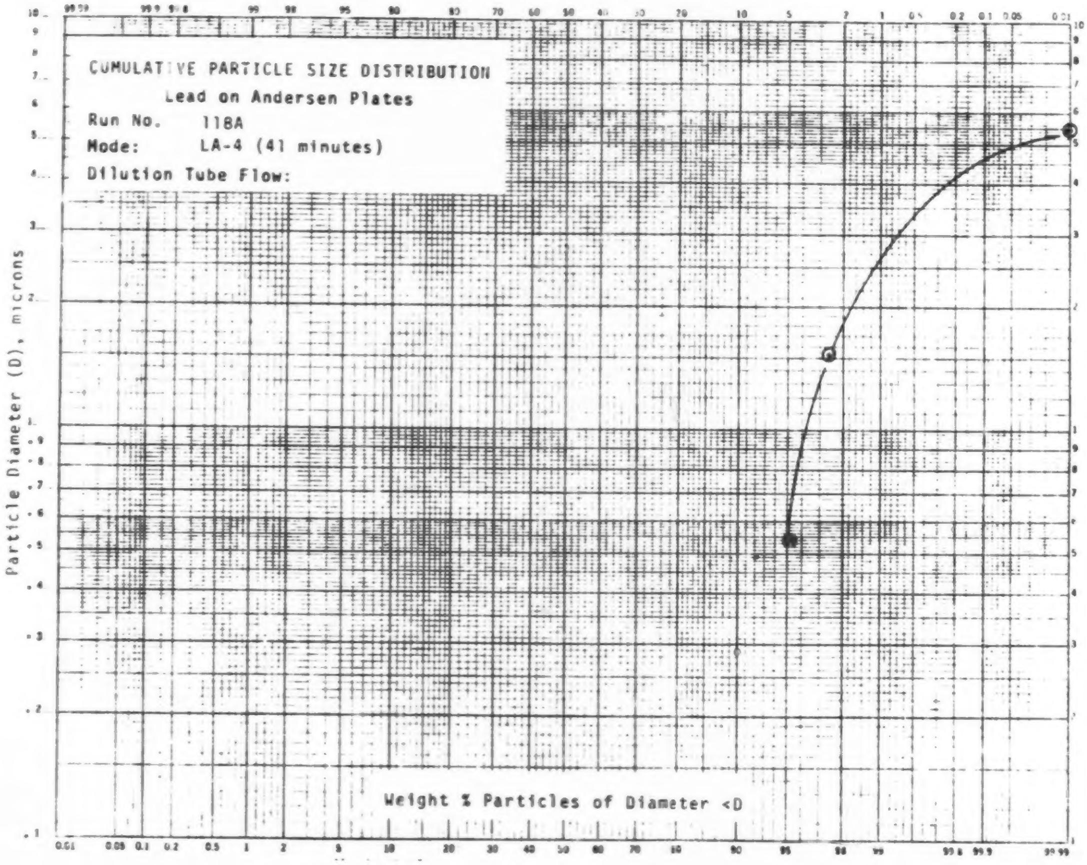

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Lead on Andersen Plates
Run No. 133B
Mode: 60 mph, SS
Dilution Tube Flow:


CUMULATIVE PARTICLE SIZE DISTRIBUTION
Lead on Andersen Plates
Run No. 137B
Mode: 60 mph, SS
Dilution Tube Flow:
Particle Diameter (D), microns
Weight % Particles of Diameter <D

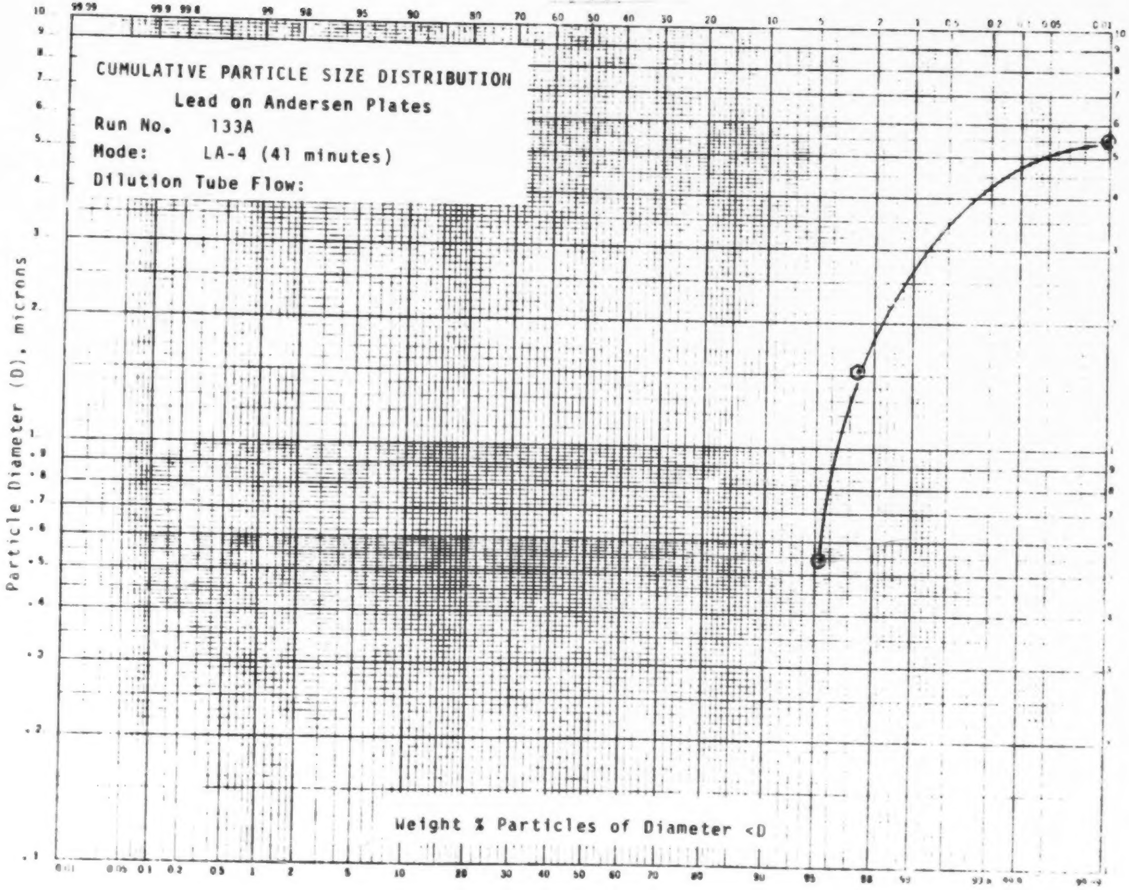

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Lead on Andersen Plates
Run No. 174C
Mode: 60 mph, SS
Dilution Tube Flow:
Particle Diameter (D), microns
Weight % Particles of Diameter <D



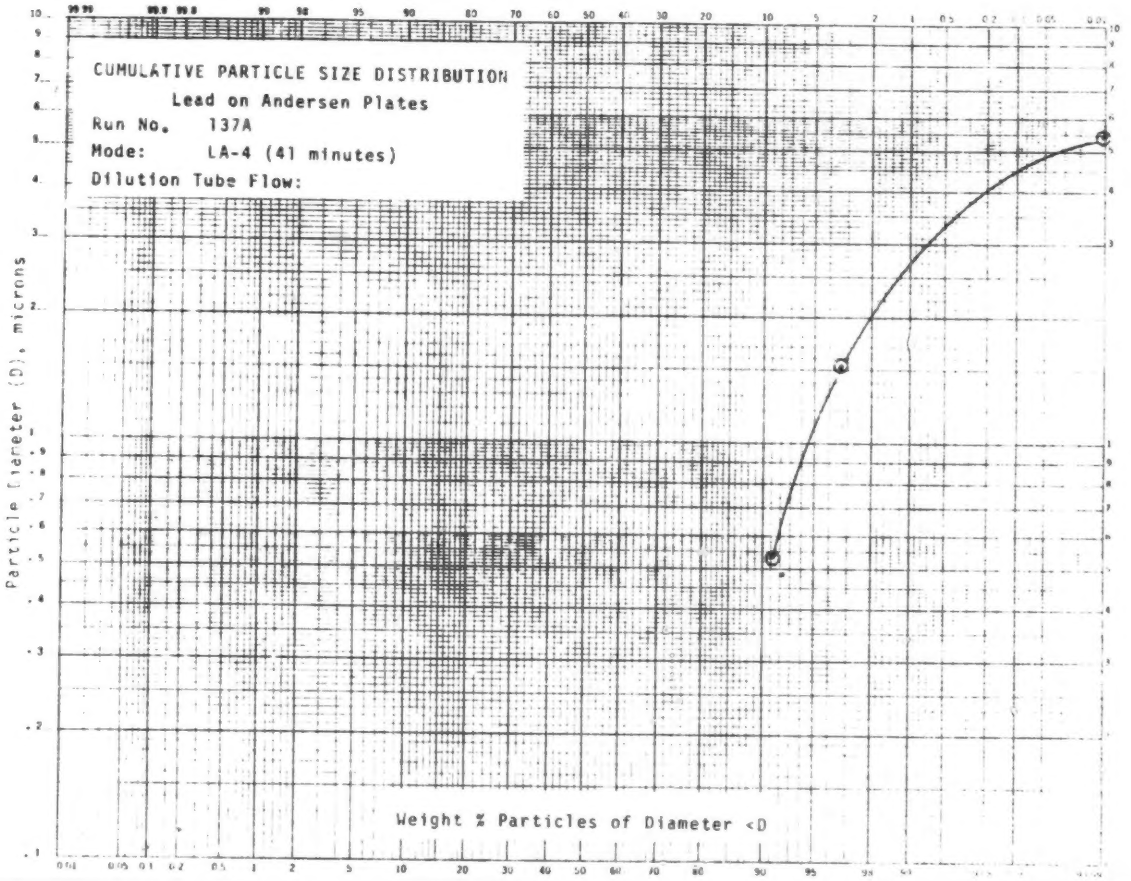
CUMULATIVE PARTICLE SIZE DISTRIBUTION
Lead on Andersen Plates
Run No. 124A
Mode: LA-4 (41 minutes)
Dilution Tube Flow:



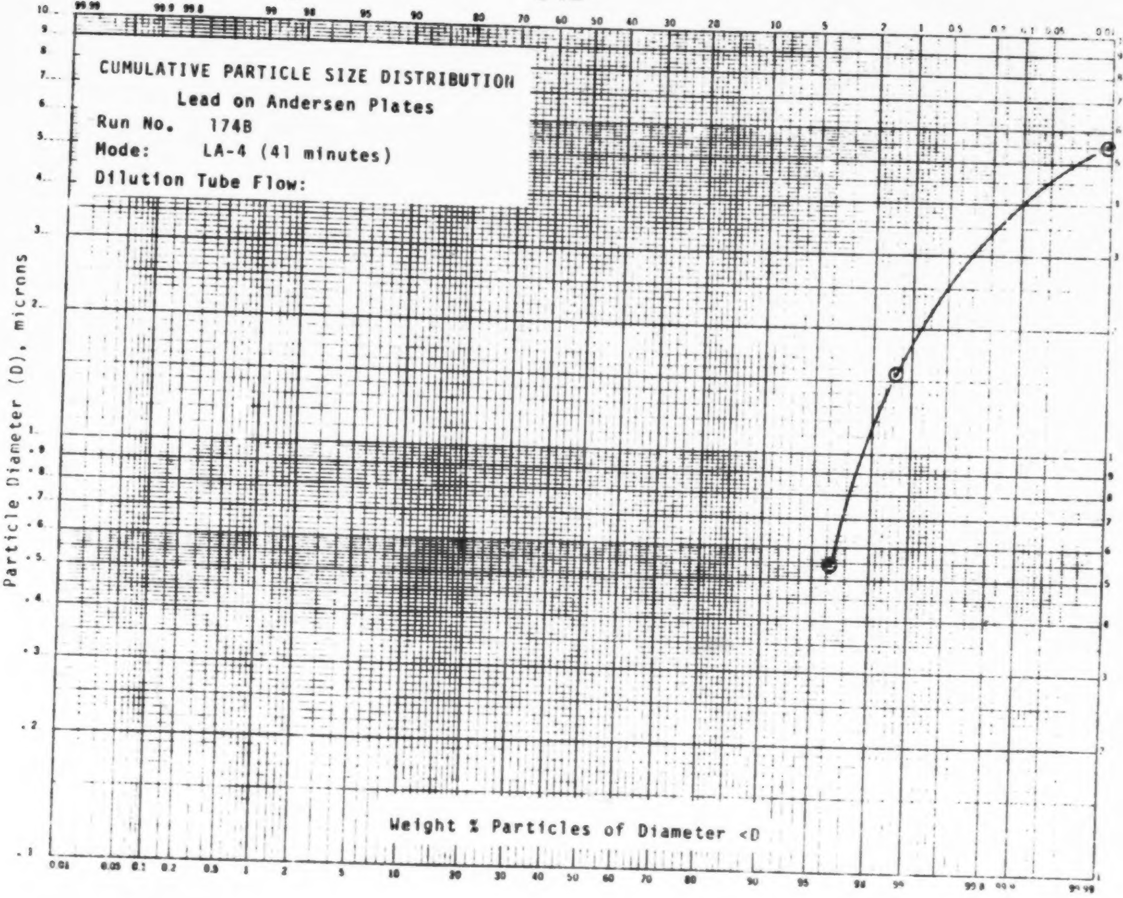
CUMULATIVE PARTICLE SIZE DISTRIBUTION
Lead on Andersen Plates
Run No. 118A
Mode: LA-4 (41 minutes)
Dilution Tube Flow:

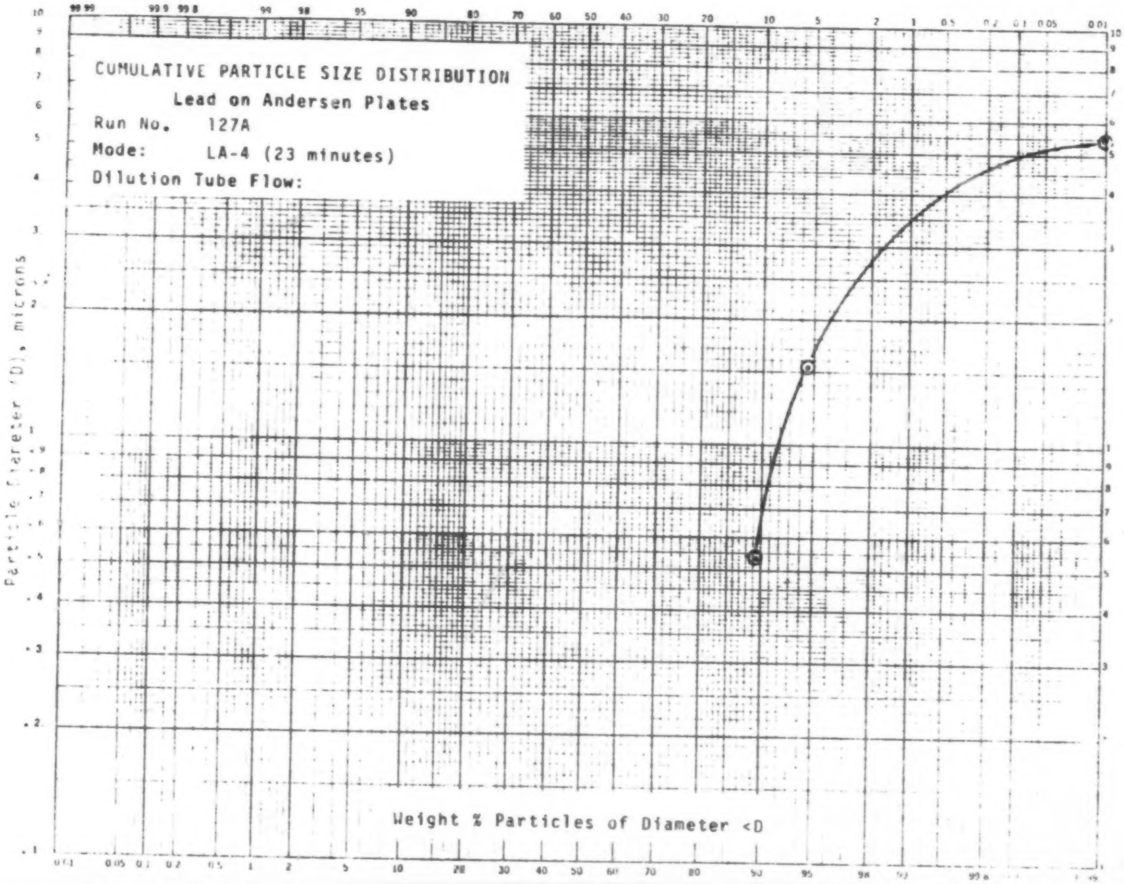


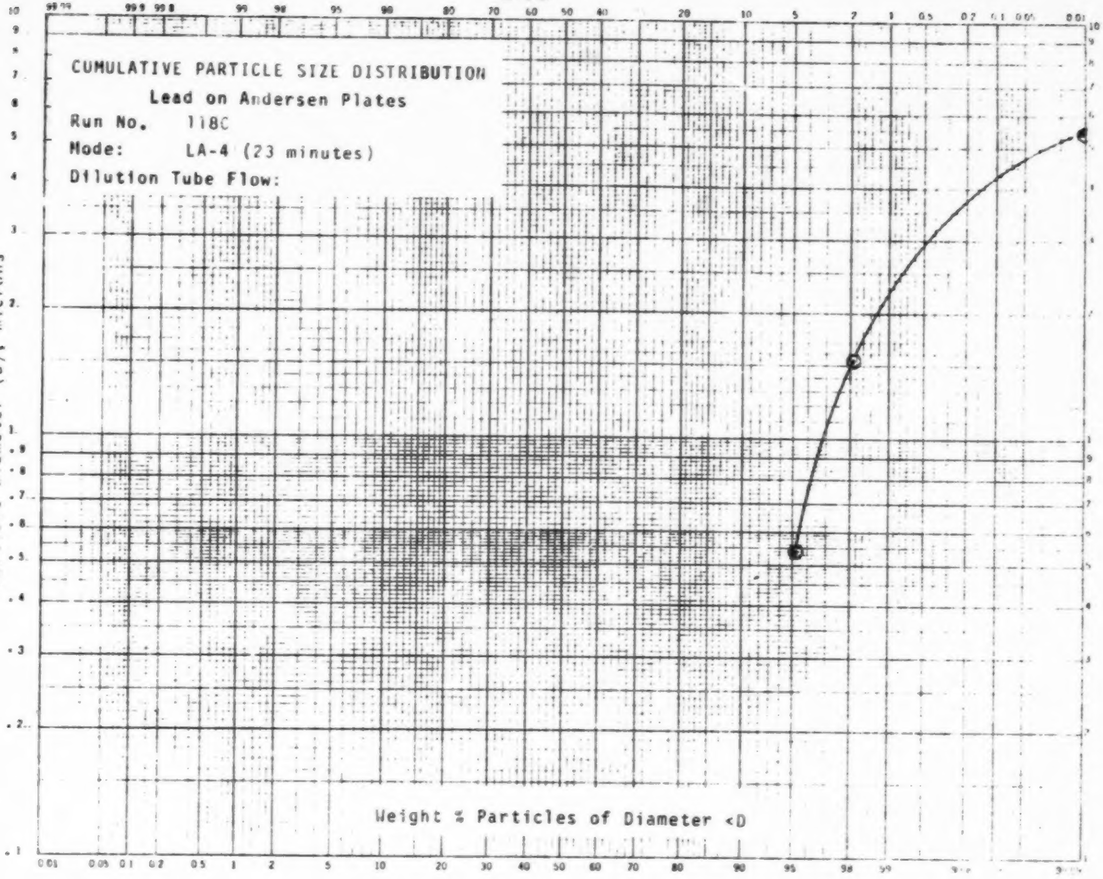
CUMULATIVE PARTICLE SIZE DISTRIBUTION
Lead on Andersen Plates
Run No. 133A
Mode: LA-4 (41 minutes)
Dilution Tube Flow:



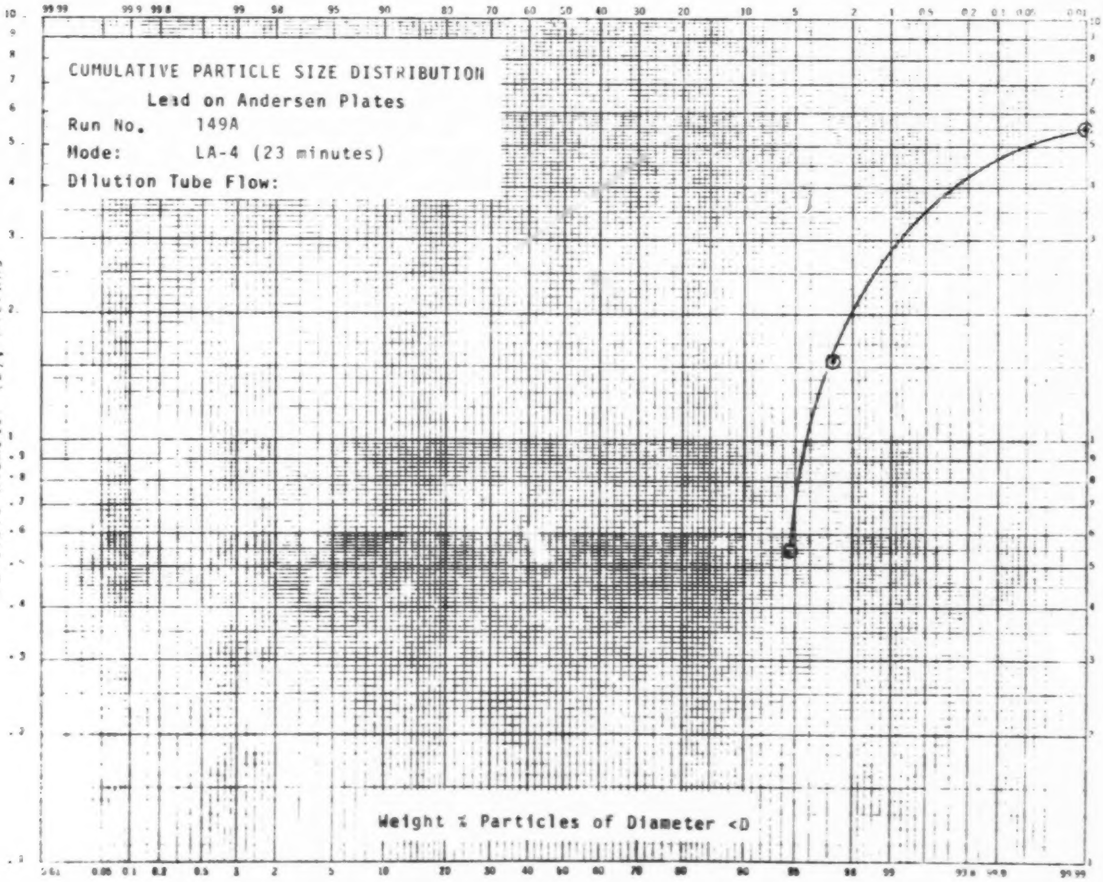
CUMULATIVE PARTICLE SIZE DISTRIBUTION
Lead on Andersen Plates
Run No. 137A
Mode: LA-4 (41 minutes)
Dilution Tube Flow:


CUMULATIVE PARTICLE SIZE DISTRIBUTION
Lead on Andersen Plates
Run No. 174B
Mode: LA-4 (41 minutes)
Dilution Tube Flow:
Particle Diameter (D), microns
Weight % Particles of Diameter <D

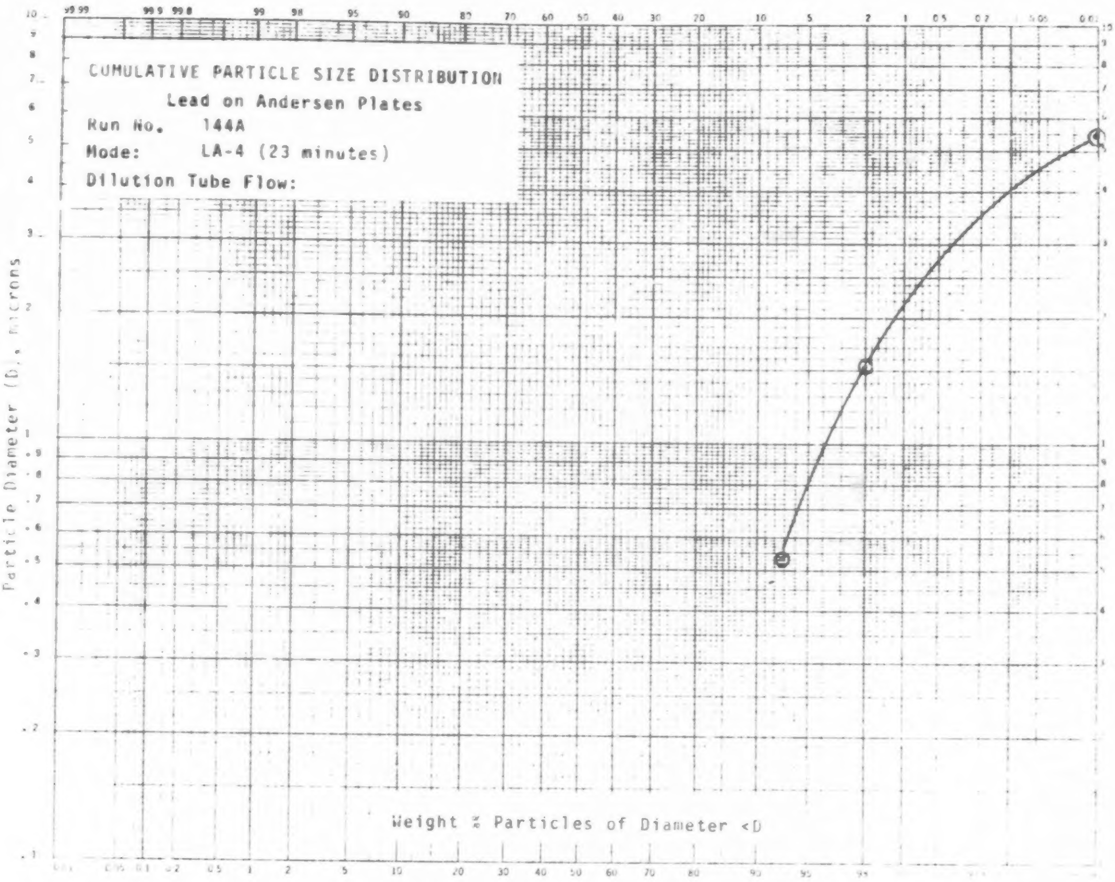

CUMULATIVE PARTICLE SIZE DISTRIBUTION
Lead on Andersen Plates
Run No. 127A
Mode: LA-4 (23 minutes)
Dilution Tube Flow:
Particle Diameter (D), microns
Weight % Particles of Diameter <D



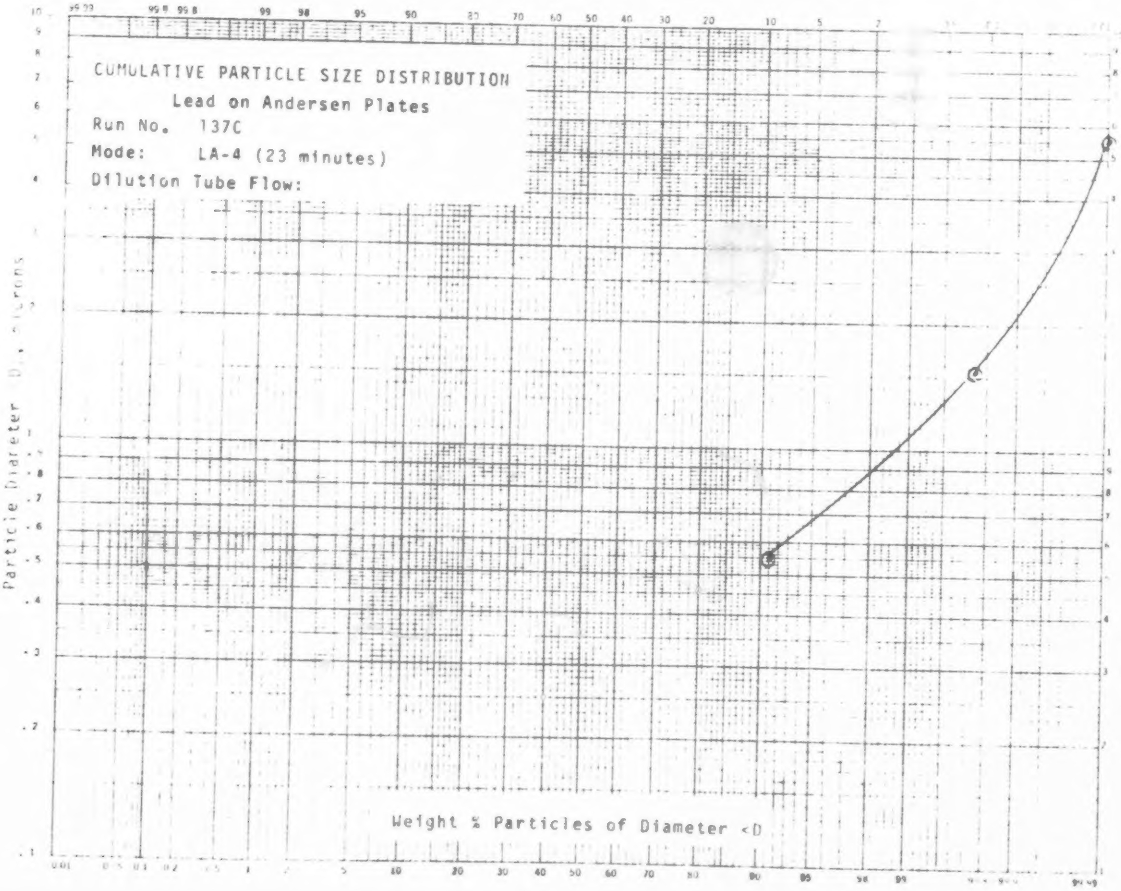
CUMULATIVE PARTICLE SIZE DISTRIBUTION
Lead on Andersen Plates
Run No. 118C
Mode: LA-4 (23 minutes)
Dilution Tube Flow:



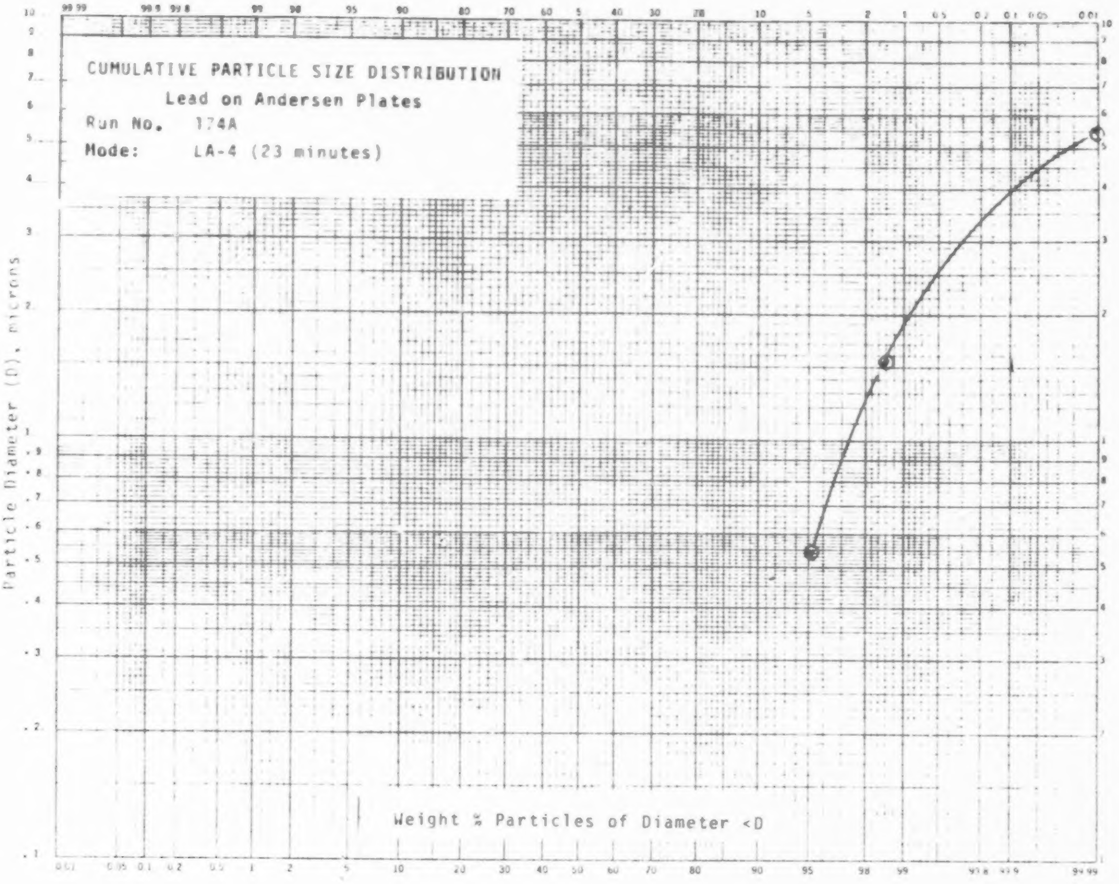
CUMULATIVE PARTICLE SIZE DISTRIBUTION
Lead on Andersen Plates
Run No. 149A
Mode: LA-4 (23 minutes)
Dilution Tube Flow:



CUMULATIVE PARTICLE SIZE DISTRIBUTION
Lead on Andersen Plates
Run No. 144A
Mode: LA-4 (23 minutes)
Dilution Tube Flow:



CUMULATIVE PARTICLE SIZE DISTRIBUTION
Lead on Andersen Plates
Run No. 137C
Mode: LA-4 (23 minutes)
Dilution Tube Flow:


CUMULATIVE PARTICLE SIZE DISTRIBUTION
Lead on Andersen Plates
Run No. 174A
Mode: LA-4 (23 minutes)
Particle Diameter (D), microns
Weight % Particles of Diameter <D
10
9
8
7
6
5
4
3
2
1
.9
.8
.7
.6
.5
.4
.3
.2
.1
0.01
0.05
0.1
0.2
0.5
1
2
5
10
20
30
40
50
60
70
80
90
95
98
99
99.8
99.9
99.99